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Thermal hydrolysis and structure studies on cobalt (II) acetate

Russell J. Hesch

THERMAL HYDROLYSIS AND STRUCTURE STUDIES ON COBALT (II) ACETATE

BY

Russell J. Hesch

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Approved by

W. P. Jeffreys (advisor) D. R. Edwards

H. O. McDonald S. J. Pagano

ABSTRACT

The investigation of dehydration of hydrated cobalt (II) acetate, as prescribed by various authors, shows that dehydration is accompanied by partial hydrolysis to form at least two different basic acetates with rough formulas of $Co_4(C_2H_3O_2)_7OH$, purple and $Co_5(C_2H_3O_2)_8(OH)_2$, pink. This thermolysis data is in partial agreement with other recently published results.

Evidence is presented which shows that Mallinckrodt's analytical reagent is $Co(C_2H_3O_2)_2 \cdot 2H_2O$, rather than $Co(C_2H_3O_2)_2 \cdot 4H_2O$.

The determination of the structure of cobalt (II) acetate precipitated from glacial acetic acid was approached by infrared studies, preparation of adducts and magnetic susceptibility measurements. It was found that the cobalt (II) acetate dimer formed in glacial acetic acid is octahedrally coordinated with two coordination sites vacant. It was shown that the binuclear cage structure common to Cu(II), Cr(II) and Rh(II) acetates is the probable structure of cobalt (II) acetate dimer, $Co_2(C_2H_3O_2)_4$. The primary basis for this conclusion was the infrared studies.

Strong evidence is presented indicating that cobalt (II) acetate exists in three distinct structural orientations: $Co(C_2H_3O_2)_2 \cdot 4H_2O$, unidentate acetates with bonding mainly ionic in character; $Co(C_2H_3O_2)_2 \cdot 2H_2O$, bidentate acetates with single metal atoms and also the possibility of some binuclear bridging acetates; $Co_2(C_2H_3O_2)_4$, binuclear cage structure with bridging acetates.

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I. INTRODUCTION

The object of this study was to investigate the structure of cobalt (II) acetate, isolated from glacial acetic acid, without recourse to standard x-ray methods.

Prior to 1930 investigators reported widely varying results for the solubility of cobalt (II) acetate in acetic acid (1,2). These investigators and others (3,4,5) had observed what they described as a silken turbidity or powdery sludge. However, no serious attempt was made to identify the structure of this material.

A specie of cobalt (II) acetate from anhydrous acetic acid was found to have two metal atoms in its molecular unit and was described by Tappmeyer and Davidson (3) as a hemisolvate. Since copper (II), chromium (II) and rhodium (II) acetates are known to be dimeric (6,7,8) in the solid state, cobalt (II) acetate was believed to change to a dimeric structure in anhydrous acetic acid. Freezing point data from the literature (3,9) approached behaviour predicted for dimer units, and kinetic data (4) required a dimer specie to explain the reaction between cobalt (II) and lead (II) acetates in acetic acid, lending further support to the dimer postulate.

The common method to prepare an anhydrous salt is to heat the hydrated salt. This method has been widely applied to cobalt (II) acetate tetrahydrate (3,10,11) and it is stated in the Handbook of Chemistry and Physics and in Lange's Handbook of Chemistry that four water molecules are lost at 140°C.

A simple weight loss determination showed this to be substantially incorrect and gave rise to the study of cobalt (II) acetate tetrahydrate thermal decomposition.

Two formula abbreviations are used throught this work. The first is an abbreviation for the acetate radical $(C_2H_3O_2)^-$, which is presented in formulas as $(OAc)^-$. Ethylenediamine ($NH_2CH_2CH_2NH_2$) is abbreviated in formulas as (en).

II. REVIEW OF THE LITERATURE

A. THERMAL DEHYDRATION AND HYDROLYSIS OF COBALT (II) ACETATE.

No exact data for dehydration by heating exists in the literature except that the Handbooks of Chemistry and Physics state that cobalt (II) acetate tetrahydrate, $Co(OAc)_2 \cdot 4H_2O$, loses its water at 140°C. Similarly, others have described the dark purple or violet salt, obtained by heating the tetrahydrate, as being anhydrous cobalt (II) acetate (3,10).

Wilke and Opfermann (12) studied the thermal discoloring of cobalt salts and described the acetate reaction as dehydration and decomposition. The tetrahydrate of cobalt (II) acetate is classified as a violet salt which dehydrates at 95°C forming a blue-violet salt. Further dehydration and decomposition occures at 170°C yielding an indistinct black-gray material.

Blanchard (10) prepared what he called anhydrous cobalt (II) acetate from commercial cobalt (II) acetate tetrahydrate. After purification by several recrystallizations from fifty percent aqueous acetic acid, the product was "dehydrated" by vacuum pumping at 80°C and 1 mm. Hg for 60 hours. Standard solutions of the anhydrous salt were prepared in anhydrous acetic acid and in all cases were shown by Karl Fisher titration to contain less than 0.01% water.

Liecester and Redman (11) reported that attempts to dehydrate cobalt (II) acetate tetrahydrate at 110°C resulted in the formation of some basic salt. Therefore, they prepared anhydrous cobalt (II) acetate by refluxing the basic salt with excess of acetic anhydride. The cobalt content

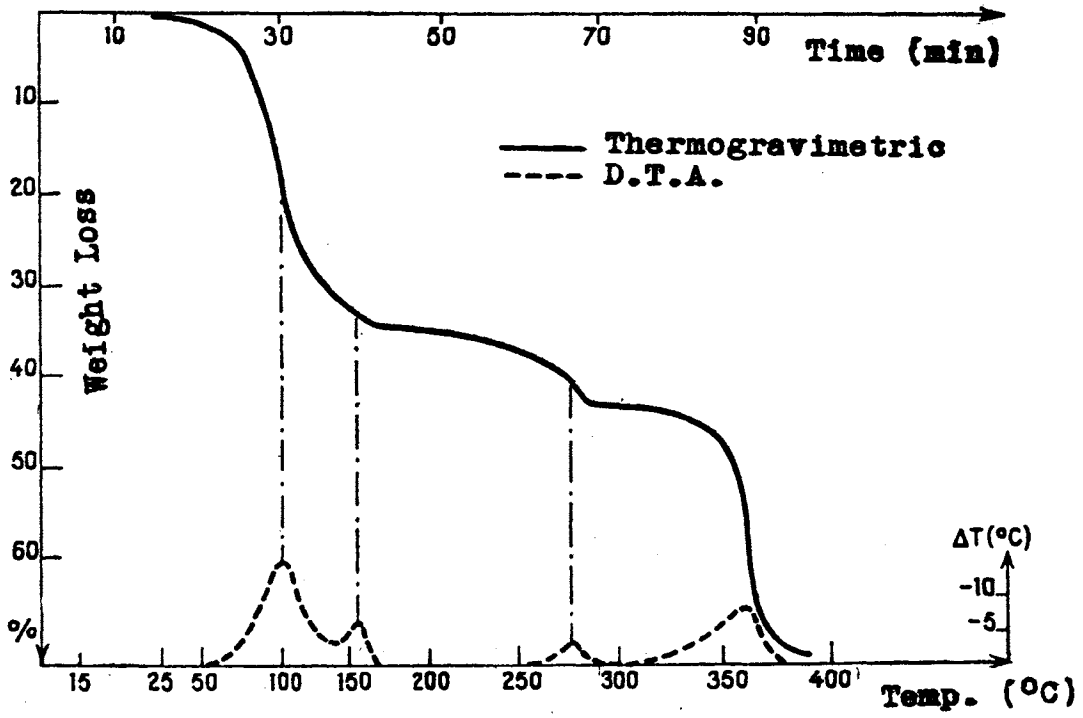

Figure I: Thermolysis of Cobalt (II) Acetate (13).

of this compound was reported as 32.8%. The anhydrous material was then used to study thermal decomposition.

Doremieux and Boulle (13) first published data on the thermal decomposition of cobalt (II) acetate tetrahydrate in July 1963 and Doremieux (14) published additional data one year later.

Their thermogravimetric and temperature differential data (Figures I & II) show evidence of several probable intermediates before the final formation of cobalt (II) oxide. It was further determined that hydrolysis of the acetates by water of hydration occurred simultaneous with dehydration and that dehydration was complete at a temperature of 120°C. At temperatures above this only acetic acid was detected as a gaseous product.

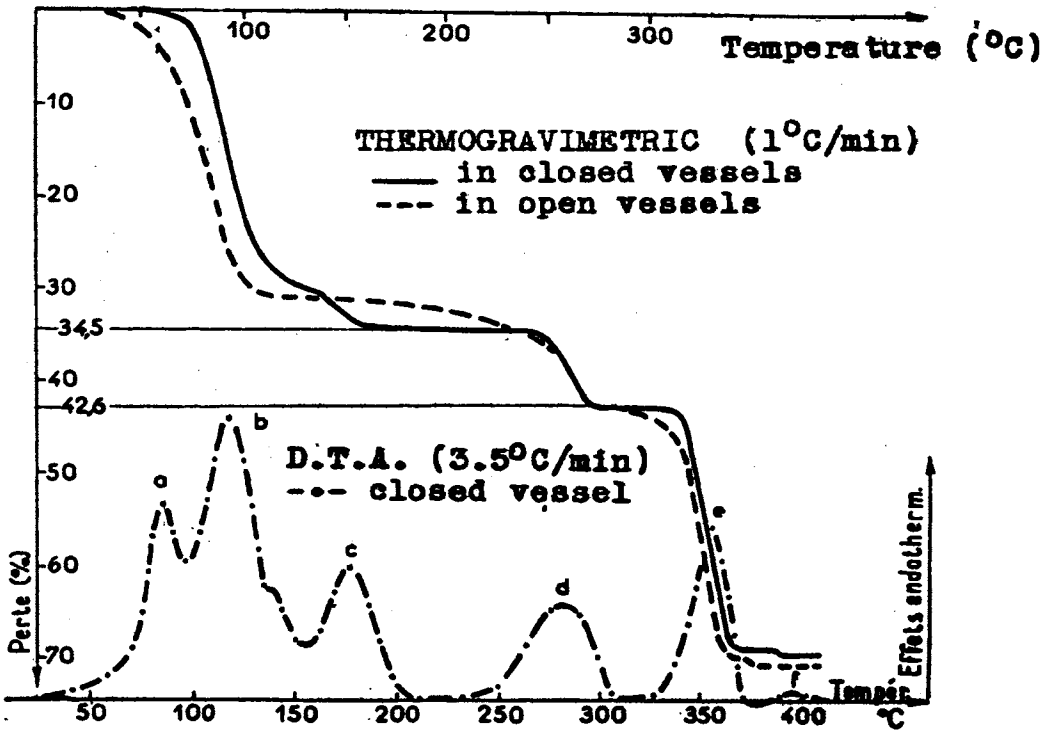

Figure II: Thermolysis of Cobalt (II) Acetate Tetrahydrate in Open and Closed Vessels (14).

While differential thermal analysis (DTA) of cobalt (II) acetate tetrahydrate in closed vessels (Figure II) shows evidence of as many as five intermediates, Doremieux (14) has tentatively identified three new compounds. The extended plateau at 42.6% weight loss (Figure II) represents a compound which forms at temperatures between 270°-300°C. On the basis of chemical analysis and infrared spectra, Doremieux assigned a rough formula of $Co_3O(OAc)_4$ to this compound. It was described as rose colored needles that were assembled radially, looking somewhat like a sea urchin. The compound corresponding to the plateau at 34.5% weight loss in Figure II was described as rosy crystals and assigned the rough formula $Co_3(OAc)_5OH$. The third new compound identified during the thermolysis in closed vessels was cobalt (II)

acetate dihydrate.

In addition to the basic acetate $Co_3O(OAc)_4$, the only compound isolated from thermolysis in open vessels was obtained through isothermal thermolysis at 180°C. This compound was described as blue grains which appeared only in a transitory manner mixed with amorphous dehydrated acetate. A rough formula $Co_6O(OAc)_{10}$ was assigned to this material.

The result of this work shows that several basic acetates of cobalt (II) are formed when the tetrahydrate is heated. However their exact formulas have not been determined and the thermal decomposition does not occur in totally separated stages, further complicating absolute identification.

The main outcome of the work by Doremieux and Boulle was to show that dehydration of cobalt (II) acetate tetrahydrate by heating was not possible without hydrolysis to a basic acetate.

B. COBALT (II) ACETATE IN ANHYDROUS ACETIC ACID.

There has been widely differing results published as to the solubility of cobalt (II) acetate in acetic acid. Some early workers, before 1930, had reported this compound readily soluble (1) while others had reported a concentration of 0.038 N for a saturated solution at 25°C (2). It is of interest that some workers commented on a "silky turbidity" which was uneffected by temperature changes.

Proll, Sutcliffe and Walkley (5) in a study of cobalt (II) acetate ionic species in acetic acid reported that a "powdery sludge" was formed during recrystallization in acetic acid which was drastically different from crystalline

anhydrous cobalt (II) acetate. X-ray of the sludge by Debye-Scherrer powder method show the 'crystal' photograph lines as well as some new ones. The overall line spacing was consistent with a monoclinic crystal lattice. It was assumed that the "sludge" contained a different form of cobalt (II) acetate which may be a dimer or higher polymer form. This was in support of the kinetic evidence previously obtained (4). The kinetic results suggested that the dimer does not predominate and is in rapid equilibrium with the monomer. From this it was concluded that cobalt (II) exists to a slight extent in a polynuclear form in anhydrous acetic acid solutions and that a tetrahedral form, $Co(OAc)_4^{-2}$, having an absorption maximum at 565 mμ, is an important ionic specie in acetic acid.

In light of this evidence Tappmeyer and Davidson (3) made a study with the intent of identifying this residue. It was found that when a mixture containing 10-12 mole percent of cobalt (II) acetate was heated to 60°C, the dark blue salt dissolved fairly readily, giving a viscous deep blue solution which showed only a slight trace of silken turbidity and gave no immediate deposit on being cooled even to 0°C. However, when such a solution was allowed to stand for 3-4 days at room temperature, or for a few hours at 60°C, a voluminous deposit of a pink solid was formed. Samples of this substance separated by filtration from five different solutions and dried, yielded on analysis 26.3% to 31.0% (mean 28.5%) cobalt; calculated for $Co(OAc)_2 \cdot \frac{1}{2}HOAc$, 28.47%. In view of the considerable spread of the individual values, the close agreement was clearly accidental; nevertheless,

it seemed fairly certain that the pink compound was indeed a hemisolvate.

Liecester and Redman (11) may have isolated the same compound from reflux of a basic salt of cobalt (II) acetate with an excess of acetic anhydride (see page 3, this work). The basic salt which they described was apparently the same material which Tappmeyer and Davidson (3) refer to as anhydrous cobalt (II) acetate.

The item of major interest here, assuming Liecester (11) and Tappmeyer (3) isolated the same compound, is that they present the only cobalt analysis for this specie. Tappmeyer reports a mean cobalt content of 28.5% and Liecester reports a cobalt content of 32.8%. Liecester and Redman did not report the analytical system used, so no comparison of relative accuracy could be made.

C. STRUCTURES OF FIRST TRANSITION METAL ACETATES.

While investigating the crystal structure of chromium (II) acetate, van Niekerk and Schoening (6) noticed that the space group and unit-cell dimensions were closely related to corresponding data for copper (II) acetate. Since chromium (II) acetate is unstable and difficult to handle, preliminary investigations on the copper (II) acetate sister compound were studied to obtain information which could be related to the chromium (II) acetate. Subsequent work revealed some rather interesting features, which resulted in a complete structural determination of the copper (II) acetate compound.

The molecule actually determined was copper (II)

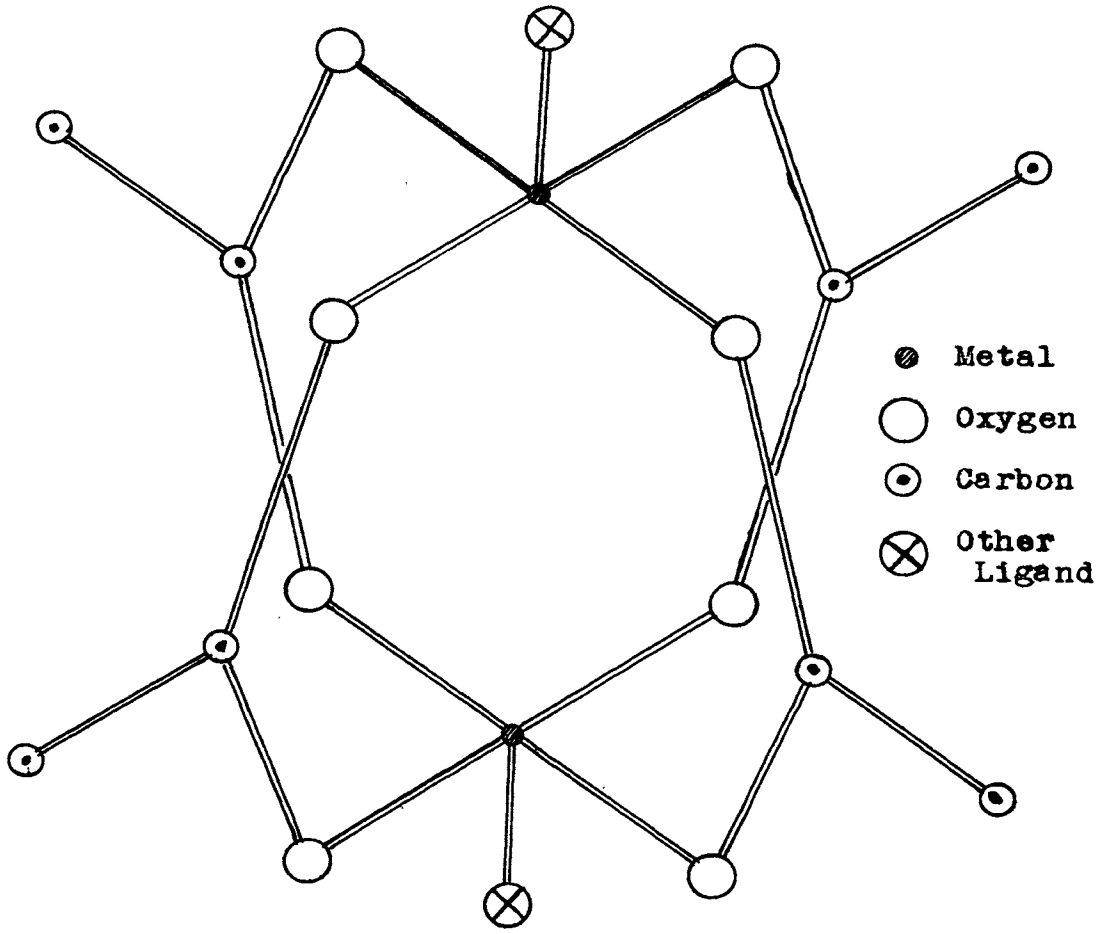

Figure III: Structure of Binuclear Caged Metal Acetate.

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acetate monhydrate. X-ray data, Fourier analysis data, and subsequently, Patterson and Harker projections were constructed for the compound. The electron density projections showed the molecule to be binuclear (Figure III). The unusual point of this work was the discovery that the copper-copper distance was abnormally short, 2.64 angstroms as compared with a value of 12 angstroms expected for the usual copper compound. It was concluded that there must be direct metal to metal bonding, although previous studies of copper compounds showed no direct bond between the central metal atoms.

In the same year van Niekerk, Schoening and deWet (7) determined the structure of chromium (II) acetate. It was

found to have the same binuclear structure as that of the copper (II) acetate. Again the extremely short metal to metal distance was observed.

Still later that same year van Niekerk and Schoening (15) reported on the structure of nickel (II) acetate tetrahydrate and cobalt (II) acetate tetrahydrate. Both were found to be monomers having octahedral coordination with the acetate groups trans to each other. They were determined to be isostructural, and it was concluded from the carbon to oxygen bond distances that the structure is mainly ionic in character.

Zinc (II) acetate dihydrate structure was determined by van Niekerk, Schoening and Talbot (16) through x-ray analysis. It was found to contain bidentate acetates, in separate planes orientated at 85° to each other, and two waters in a very badly distorted octahedral configuration. The individual atomic distances indicated that the nature of the metal-acetate bonds are mainly ionic in character.

D. CRYOSCOPIC WORK.

Baird (9) in his study of the nickel (II) acetate-acetic acid system resolved freezing point data collected by Davidson and Chappel (17). Additional comparative data was used to show the relationship between cobalt (II), copper (II) and nickel (II) acetates. The cobalt (II) acetate dimer freezing point data was published by Tappmeyer and Davidson (3), while the copper (II) acetate freezing point data was determined by Baird (9) in connection with the nickel (II) acetate investigation.

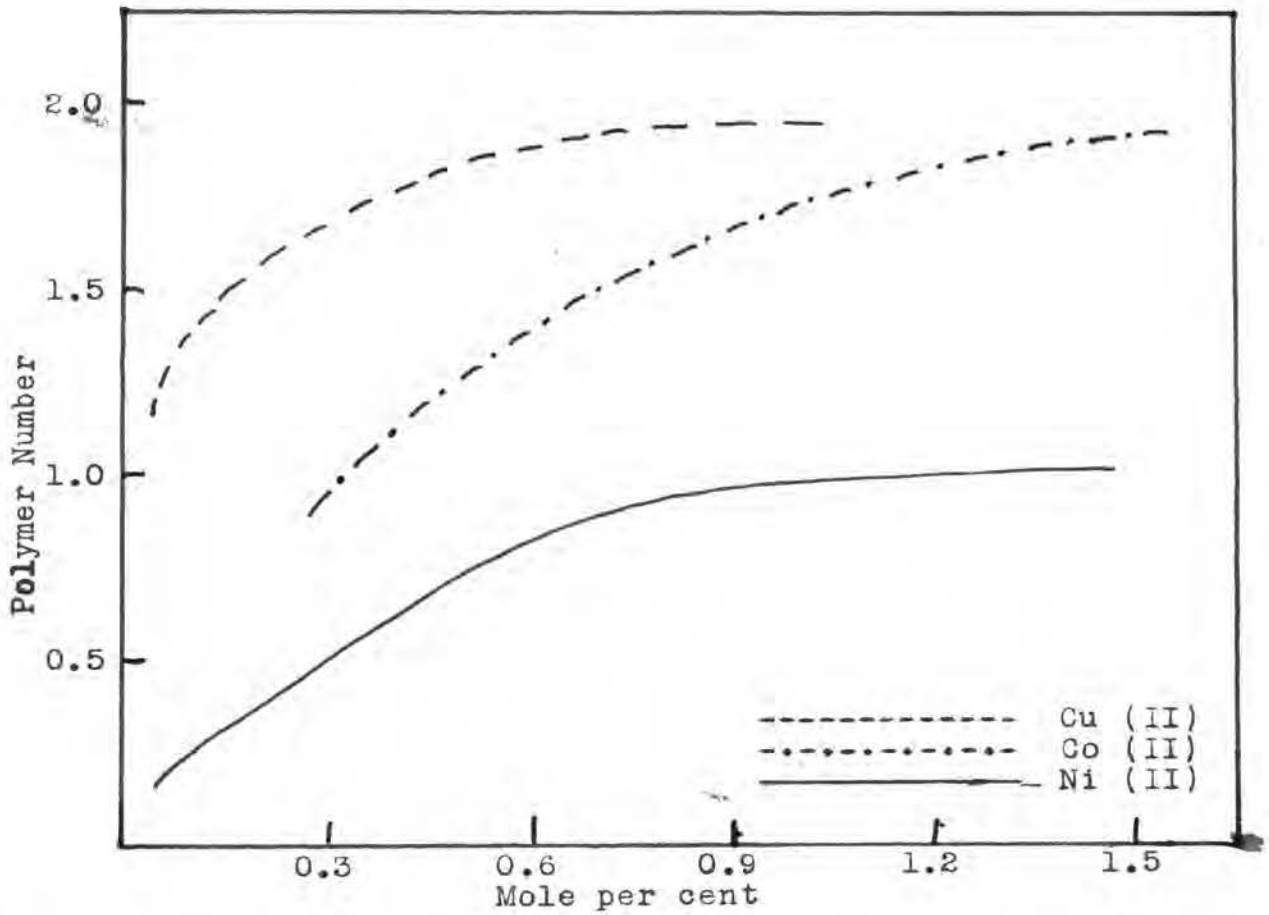
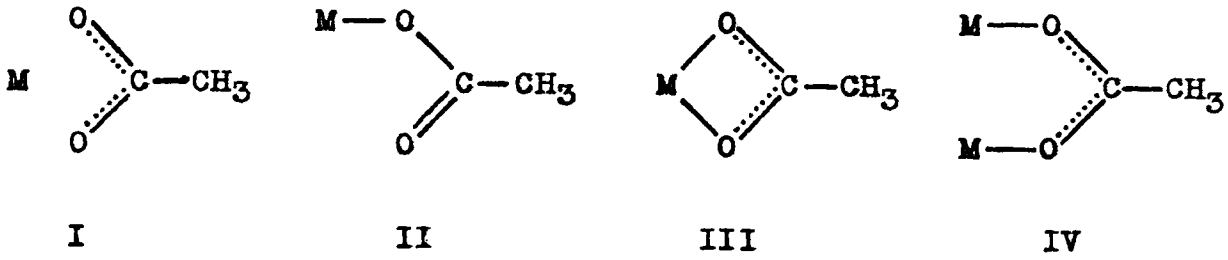


Figure IV: Polymer Number vs. Mole Percent from Freezing Point Depression by Metal Acetates in Acetic Acid.

Figure IV shows the results of these workers after the data was converted to polymer number, n, and plotted versus mole percent. The copper (II) acetate is known to be dimeric in the solid state (6) and was expected to approach a polymer number of two with increasing concentration. This proved to be true for copper (II) acetate, and cobalt (II) acetate seemingly also approaches a dimer structure, while the nickel (II) acetate appears to be limited to a monomer unit.

E. INFRARED SPECTRA OF METAL ACETATES.

The infrared spectra of many acetates have been reported and discussed (18,19,20) with primary emphasis by the spec-



I II III IV

Figure V: Methods of Acetate Anion Coordination with a Metal.

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troscopists on the position of the symmetric and asymmetric stretching frequencies of the carboxlic group.

Nakamoto (18) shows some relationships between the different types of structures (Figure V) but no metal ion has been isolated in more than one configuration, so that the effect of such a change on symmetric and asymmetric frequencies is not proposed. The shifting of symmetric and asymmetric bands is most closely associated with changing metal atoms and the relative strength of the metal-oxygen bond.

Vratney, Rao and Dilling (19) made a comparative study of fifteen acetates using either Mallinckrodt or Baker reagent chemicals, and tentatively identify most of the absorption bands involved. Of particular interest is a comparison of three absorption bands found in all metal acetates (Table I):

(1) The band around 6.3 microns due to the asymmetrical stretching motion.

(2) The band around 7.1 microns caused by the symmetrical stretching mode.

TABLE I

Infrared Absorption Bands of Metal Acetates*

Metal Ion	Wavelength in Microns Asymmetric COO	Symmetric COO	Acetate Doublet**
Ca (II)	6.3	6.8	9.5< 9.7
Ba (II)	6.2	7.1	9.6< 9.8
Zn (II)	6.4	6.9	9.5< 9.8
Cd (II)	6.3	7.0	9.5< 9.8
Co (II)	6.4	7.2	9.6≪9.8
Cu (II)	6.2	7.0	9.5 = 9.7
Cr (II)	6.3	6.9	9.5 = 9.7

*Mull spectra of normal hydrates (19).
**Relative intensity as indicated.

(3) The two bands in the region of 9.5-9.8 microns that are characteristic of the acetate group.

The bands described as "characteristic of the acetate group" are believed to be in some manner connected with the metal acetate bonding.

Considering the acetates of proven structure, a comparison can be made between the acetates of copper (II), cobalt (II), chromium (II) and zinc (II). The alkaline earths, calcium and barium, have not been studied for structural detail, but are expected to have ionic bonding, structure I (Figure V). Zinc (II) acetate is proven (16) to have structure III, but the bonding is mainly ionic in character. Cobalt (II) acetate tetrahydrate has structure II (15), but the bonding is mainly ionic, as with zinc (II) acetate. Copper (II) and chromium (II) acetates (6,7) both have structure IV.

Examination of the acetate group absorption bands reveal that the acetates with mainly ionic bonding, regardless of the coordination mode, have a doublet in which the lower wavelength band has a lower intensity than the higher wavelength band, and these two bands are at approximately 9.5 microns and 9.8 microns. Cobalt (II) acetate tetrahydrate is the only one that does not appear to fit this pattern. However, it will be shown during the course of this study that Vratney, Rao and Dilling (19) did not measure the spectrum of the tetrahydrate but used instead the dihydrate, $Co(OAc)_2 \cdot 2H_2O$ and that cobalt (II) acetate tetrahydrate does fit the pattern of "mainly ionic bonding" between acetate and divalent metals. The only two first transition metal acetates with structure IV (Figure V), copper (II) acetate and chromium (II) acetate (6,7), are observed to have acetate group absorption bands which coincide in wavelength and that the two bands are of equal intensity.

F. ADDUCTS.

Baird (9), in his study of the nickel acetate-acetic acid system, prepared adducts of the nickel (II) acetate hemiacetate in order to obtain information as to the number of coordination sites available in the structure. With this information, certain structures for the hemiacetate could be eliminated as inconsistent with the data and other structures would be given added support.

The procedures used by Baird (9) in the adduct preparation were parallel to the methods outlined by Johnson, Hunt and Neumann (21) in the study of rhodium (II) acetate. When

investigating adduct formation with a liquid material, approximately 75 mg. of finely powdered acetate was placed in a microcrucible and covered with several drops of the potential ligand. The excess liquid was allowed to evaporate; the crucible was then weighed and placed under vacuum for one hour, after which its weight was again determined. If no appreciable weight loss took place upon evacuation, the adduct formed (if any) was considered stable. Each adduct was then heated in an oven at 120°C until constant weight was achieved.

Reaction of the acetates with a gaseous material was carried out by passing a stream of the gas over a microcrucible or through a U-tube containing about 75 mg. of the finely powdered complex until constant weight was achieved. In both studies, ethylenediamine was carried on a stream of air at room temperature after it was found that treatment with the liquid resulted in other than simple adduct formation. The samples were then weighed, placed under vacuum for one hour, re-weighed and then heated at 120°C until constant weight was achieved to assure reversibility of the reactions.

Johnson, Hunt and Neumann (21) found that all ligands which formed adducts with rhodium (II) acetate gave a ratio of one dimer to two ligands, as was expected since the structure had been previously shown in an x-ray study (8). Adducts were formed by both oxygen and nitrogen coordinating compounds.

Baird (9) noted that, in cases where adducts were formed

with nickel (II) acetate hemiacetate, two unidentate ligands added per nickel dimer. Reactions other than addition were noted with ammonia and ethylenediamine. It was also noted that only nitrogen containing ligands formed adducts.

G. MAGNETIC SUSCEPTIBILITY MEASUREMENTS.

Moreau and Vatteroni (22) prepared and measured the magnetic susceptibilities of cobalt (II) alkanoates. These results are listed below in Table II.

TABLE II

Magnetic Moments of Cobalt (II) Alkanoates*

Formula	Molar Susceptibility $\chi_m \times 10^6$	Magnetic Moments (B.M.)
$Co(CHO_2)_2 \cdot 2H_2O$	10,480	4.98
$Co(C_2H_3O_2)_2$	11,090	5.14
$Co(C_2H_3O_2)_2 \cdot 4H_2O$	13,230	5.60
$Co(C_3H_5O_2)_2 \cdot 3H_2O$	14,210	5.81
$Co(C_4H_7O_2)_2$	10,760	5.24
$Co(C_5H_9O_2)_2$	12,270	5.40
$Co(C_6H_{11}O_2)_2$	9,850	4.83
$Co(C_7H_{13}O_2)_2$	11,740	5.27
$Co(C_9H_{17}O_2)_2$	12,690	5.48

*Temperature + 20°C.

Bhatnagar, Khanna and Nevgi (23) reported the magnetic susceptibilities and magnetic moments of several organic salts of nickel (II) and cobalt (II). The anhydrous

acetates were reported as follows: Cobalt (II), corrected molar susceptibility, 10,380 x 10^{-6} and magnetic moment, 5.31 B.M. at 30°C; Nickel (II), corrected molar susceptibility, 4,424 x 10^{-6} and magnetic moment, 3.03 B.M. at 38°C.

Figgis and Martin (24) calculated magnetic moments of 1.42 and 1.39 B.M. for $Cu_2(OAc)_4 \cdot 2H_2O$ and $Cu_2(OAc)_4$, respectively. During these same magnetic studies, they calculated the strength of the copper-copper bond on the basis of the temperature dependent measurements. The calculations showed a bond strength corresponding to the lateral overlap of $3d_{x2-y2}$ orbitals. This bond is characterized as a δ-bond, and is the sole direct link between the copper atoms. However, it is so weak that it can only be maintained by the bridging acetate groups.

A theoretical discussion is also presented (24) to account for the experimentally determined fact that chromium (II) acetate is diamagnetic. This acetate is isostructural with copper (II) acetate (7). Simple chromium (II) salts display magnetic moments corresponding to four unpaired electrons. However, the close approach of chromium atoms (2.46 angstroms) in the acetate permits orbitals to overlap so that four bonds can be formed, one σ-bond, two π-bonds and a δ-bond. The overlap of orbitals is expected to be small, but is sufficiently greater than is observed in copper (II) acetate to permit electron pairing, accounting for the observed diamagnetism. The metal-metal bonding of both compounds is a result of the bridging acetate groups.

Martin and Waterman (25) obtained magnetic susceptibilities for copper (II) propionate, butyrate, laurate, stearate and behenate. The behavior closely paralleled that of copper (II) acetate, and it was concluded that all of the alkanoate salts have fundamentally identical molecular structures, consisting of the caged binuclear couple. Copper (II) formate complexes were observed to be the only compounds of this series that do not conform with the general trend.

Six varieties of copper (II) formate were prepared and their magnetic moments measured by Martin and Waterman (26). No theory for the anomalous behavior was given, although super-exchange was discussed. It was postulated that the structure of the formate salt is different from that of the other n-alkanoates due to greater electron density on the hydroxyl-oxygen atoms because of the inductive effects of the n-alkyl groups. This shift in electron density reduces the electrostatic repulsion between copper atoms sufficiently for the binuclear configuration to be favored. With the formate group, however, the residual positive charge is great enough that the bridging arrangement is not favored.

III. THERMOLYSIS OF COBALT (II) ACETATE

A. INTRODUCTION.

When attempts were made to duplicate the procedures of Tappmeyer and Davidson (3), the results obtained were in partial disagreement with their observations. This portion of the study resulted as an outgrowth of these discrepencies.

As a starting material for the study of the $Co(OAc)_2$—HOAc system they used $Co(OAc)_2$ prepared by heating $Co(OAc)_2 \cdot 4H_2O$ for two hours at 156°C. During this study, the procedure resulted in loss of weight sufficient for only half of the water, and finally lead to the postulation of $Co(OAc)_2 \cdot 2H_2O$.

Doremieux and Boulle (13,14) have studied the thermolysis of cobalt acetate tetrahydrate using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and present evidence of several basic acetate species of cobalt (II). These results were not available until after most of this study was complete. However, reasonable correlation was attained.

B. EXPERIMENTAL.

In the absence of TGA and DTA equipment, attempts were made to follow weight loss by weighing with a normal analytical balance after cooling. Cobalt (II) acetate tetrahydrate (M.W. 249.09) analytical reagent obtained from Mallinckrodt Chemical Works, St. Louis, Mo. was used for this study. Batches under three seperate control identification designations (NMB-1, YAB-1 & YMG) were used in parallel experiments.

The analytical reagent was initially heated on open watch glasses (open vessels) in 2 to 4 gram samples at temper-

atures from 120° to 160°C. When larger samples, e.g., approximately 20 grams, were heated in a similiar manner a different product was formed. This second product was subsequently prepared by heating 2 to 6 gram samples in six inch test tubes (closed vessels) over the same temperature range. Additional heating was affected with the sample under a vacuum using a sulfuric acid bath. The highest temperature utilized was 300°C. The acetic acid evolved when heating in open vessels was measured by trapping the gaseous products in a standard sodium hydroxide solution. This was accomplished by placing the sample under vacuum and heating with an oil bath to temperatures varying from 120° to 160°C. No suitable means of measuring the acetic acid from the closed vessels could be devised.

The terms open and closed vessels are not used in the literal sense in this work. When the thermolysis occurs in any vessel and the atmosphere is sufficiently restrictive to permit the gaseous products to interact with the solid sample, the vessel is defined as a "closed vessel." Therefore, thermolysis occurring under vacuum is defined as a "open vessel" because the gaseous products are removed and no interaction with the solid sample can occur.

All thermolysis products were subjected to re-hydration using distilled water and to cobalt analyses using the thiocyanate colorimetric system (Appendix I) (27,28,29). In addition to chemical analyses, infrared spectra were measured and magnetic susceptibilities determined (Appendix II).

C. RESULTS.

Heating of the analytical reagent at temperatures between 120° and 160°C yields two distinct compounds; in open vessels a dark purple or blue-purple compound, and in closed vessels a light purple or grayish-pink material. Both of these products undergo a change in crystalline form at 280°-300°C, apparently yielding the same product. The product from open vessels had a tendency to sublime after undergoing partial melting and resolidification at about 230°C. No significant tendency to sublime was observed for the products from closed vessels.

All three of these products when placed in water form a solution of cobalt (II) acetate and a precipitate of α-cobalt (II) hydroxide. The details for identification of the hydroxide are presented in Appendix III.

In forming the initial product in open vessels (dark purple) while heating in an oven, the analytical reagent underwent a very rapid weight loss, followed by a slow but apparently continous weight loss until black oxide and carbon formed (Figure VI - solid line). When the effects of oxygen were eliminated by carrying out the reaction under a vacuum, the limiting point for weight loss was determined to be 20.4% of initial sample weight (Figure VI - broken line). Cobalt analyses of the hydroxide and acetate produced by hydrolysis of the above product established an acetate/hydroxide ratio of between 5.3/1 and 6.08/1. From measurement of acetic acid evolved in the heating process an acetate/hydroxide ratio of 7.34/1 was shown.

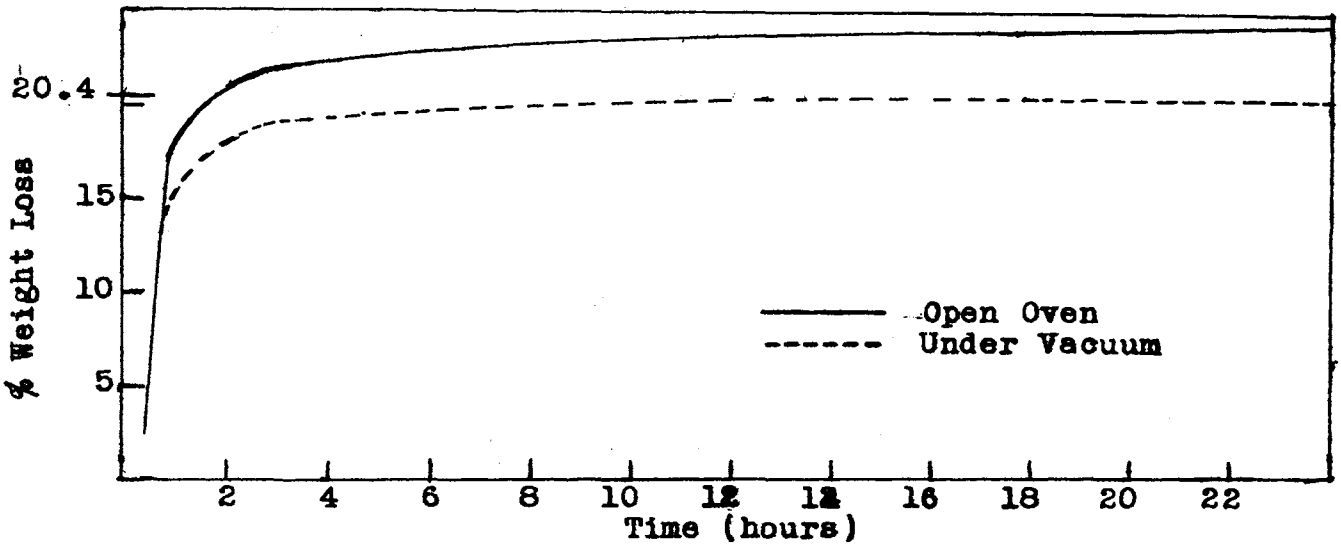

Figure VI: Weight Loss vs. Time for First Stage Thermolysis of Cobalt (II) Acetate at 135°C in Open Vessels.

The infrared spectrum of this compound showed the following major absorption bands:

Hydroxyl stretching	3.00 microns
Carboxyl asymmetric	6.45 and 6.55 microns
Carboxyl symmetric	7.15 microns
Acetate doublet	9.55≪9.75 microns
Skeletal vibration	14.90 microns (broad)

The asymmetric stretching band appeared to definitely resolve into a doublet, while the symmetric mode was identified at 7.15 microns. Furthermore, in some of the spectra, there was a possible indication of a second symmetric stretching band at 7.08 microns.

The magnetic susceptibility measurements of this first thermolysis product along with that of the two other products discussed below are listed in Table III.

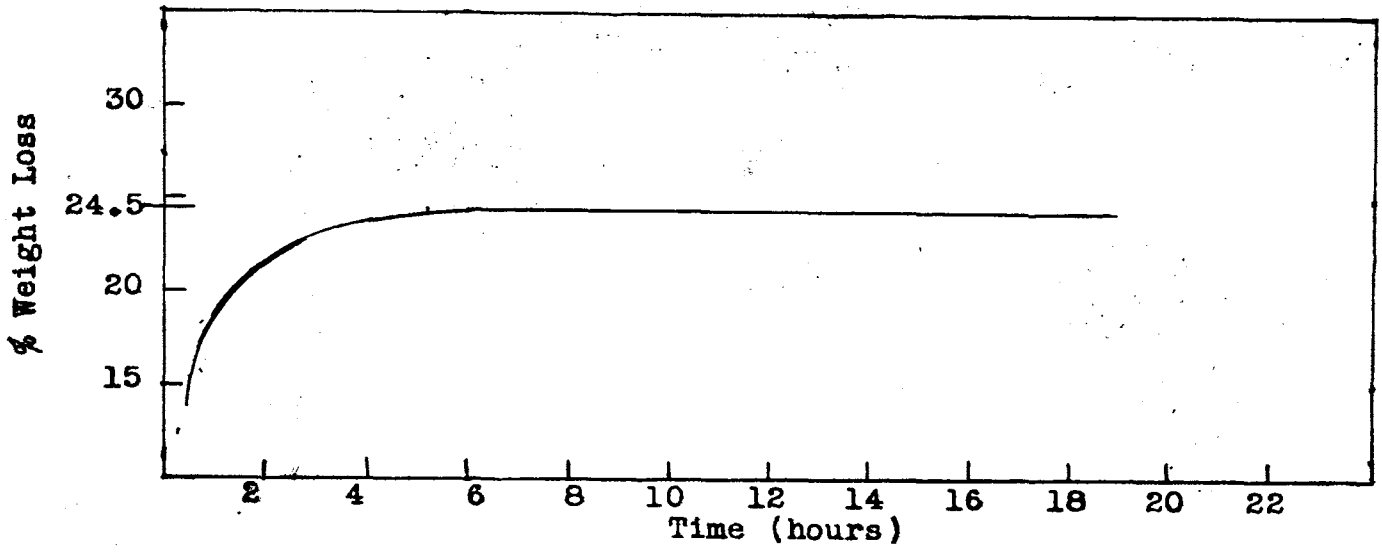

Figure VII: Weight Loss vs. Time for First Stage Thermolysis of Cobalt (II) Acetate at 140°C in Closed Vessels.

The thermolysis product obtained in closed vessels (grayish-pink) was followed on a time basis at 140°C as shown in Figure VII. The results indicate that the limit of weight loss under these conditions was 24.5% of the initial sample weight. Cobalt analyses of the hydrolysis products established an acetate/hydroxide ratio of 2.81/1. Carbon and hydrogen analyses performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England on three samples of this compound showed: 23.41% C, 3.62% H; 24.09% C, 3.77% H; and 24.13% C, 3.76% H.

The infrared spectrum of the thermolysis product obtained in closed vessels showed the following major absorption bands:

Hydroxyl stretching	2.90 microns
Carboxyl asymmetric	6.41 microns
Carboxyl symmetric	7.09 and 7.71 microns
Acetate doublet	9.50 ≪ 9.69 microns

TABLE III

Magnetic Susceptibilities of Cobalt (II) Basic Acetates

Compound	Gram Suscept. $\chi \times 10^6$	Moment* B.M.
$Co_4(C_2H_3O_2)_7OH$ purple	51.95	4.66
$Co_5(C_2H_3O_2)_8(OH)_2$ pink	52.50	4.50
$Co_3O(C_2H_3O_2)_4$ rose	Ferro-Magnetic - see Appendix II	

*Magnetic Moments based on experimental mole weights.

Unidentified doublet	10.50 ≤ 10.70 microns
Skeletal vibration	14.90 microns (broad)

The asymmetric and symmetric stretching bands were again broadened and the symmetric band must definitely be considered a doublet while the asymmetric was apparently restricted to a single band.

When either of the two products described above were heated to 280°-300°C under a vacuum, a change in crystal structure occurred. This third compound appears as crystals arranged radially and in spherical clusters. The color in bulk is dark purple, but examination with a microscope reveals rose colored needles which appear in general to be rhombic, although some specimens have delicate edges and are flattened out like a knife. The formation of this compound was also accompanied by the formation of some cobalt oxide and cobalt metal. A weight loss of 32.2% of the initial sample weight (analytical reagent) was determined for this compound. The acetate/hydroxide ratio obtained from cobalt analysis varied from about 1.50/1 to 1.78/1. These figures are definitely low in acetate due to oxide and

metal formation which occurred with this transformation. Approximately 0.21 moles of acetic acid were evolved for every mole of cobalt.

The infrared spectrum of the thermolysis product formed at 290°C showed the following major bands:

Hydroxyl stretching	2.90 microns (very minor)
Carboxyl asymmetric	6.49 microns
Carboxyl symmetric	7.17 microns
Acetate doublet	9.55≪9.71 microns
Unidentified doublet	10.27 >10.55 microns
Skeletal vibration	14.95 microns (broad)

The asymmetric and symmetric stretching modes were definitely singlets in this compound. The unidentified doublet was in the approximate same position as with the previous compound but the intensity has been reversed.

The magnetic measurements of this material show the behaviour of a ferro-magnetic substance. This was caused by the presence of metallic cobalt formed with the product. Further comment is made in Appendix II.

Examination of the above data for the first product in open vessels (Figure VI) showed that if no thermal hydrolysis occurred only three of the four moles of water present in cobalt (II) acetate tetrahydrate were removed. Therefore, Mallinckrodt's analytical reagent was analysed for cobalt content with results as shown in Table IV. The theoretical cobalt content for the tetrahydrate is 23.7% and for the dihydrate is 27.8%. Two samples were subsequently recrystallized from water and analysed for

TABLE IV

Cobalt Analyses of Mallinckrodt Analytical Reagent*

Control Identification Designation	Per Cent Cobalt
NMB-1	28.6, 28.8, 29.2
YAB-1	28.7, 28.8, 29.0
YMG	27.4, 27.7, 28.4

*Cobalt (II) acetate tetrahydrate

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cobalt content. Each sample of recrystallized material was analysed twice and showed 23.5-23.6% cobalt and 23.7-23.8% cobalt.

D. DISCUSSION.

The analysis of cobalt content in Mallinckrodt's analytical reagent, which is represented as cobalt (II) acetate tetrahydrate, is in virtual agreement with the theoretical amount of cobalt in the dihydrate. The thermolysis data shows that if the tetrahydrate is the starting material there must be approximately two moles of water present in all thermolysis products, including the product formed at 290°C and in the final product, cobalt (II) oxide (not studied in these experiments). Minimal experience in chemistry would not permit acceptance of water retention at 300°C by a metal salt of an organic acid. The infrared spectrum of the commercial reagent also shows sufficient deviation from the spectrum of the tetrahydrate (discussed in detail in a later part of this work) to indicate that they are different compounds. Therefore, it must be concluded that Mallinckrodt's reagent is misrepresented and is, in fact, cobalt (II) acetate

dihydrate, $Co(OAc)_2 \cdot 2H_2O$.

The dark purple salt obtained in the first step of the thermolysis of the dihydrate in open vessels has an experimental molecular weight of 169-170, based on the weight loss data shown in Figure VI. The acetate/hydroxide ratio, obtained from both cobalt analysis and acetic acid measurements, indicates that there is 5.5 to 7.5 acetates for every hydroxide group in this material. On this basis the rough formula $Co_4(OAc)_7OH$, M.W. 4(167) is given for this basic acetate. Doremieux (14) in his study of the thermolysis of the tetrahydrate describes what may be a corresponding compound. Doremieux described it as blue grains appearing with the amorphous dehydrated acetate during isothermal thermolysis at 180°C, and it was given the rough formula $Co_6O(OAc)_{10}$. Because of the strong O-H stretching band observed in this work it is doubtful that the same compound was characterized. The compound characterized by this study probably is part of what is called amorphous dehydrated acetate by Doremieux. This difference in results is due to the difference in starting materials.

When the heating is conducted in closed vessels so that the gaseous products influence the thermolysis, a light purple or gray-pink material is obtained, having an experimental molecular weight, from weight loss data (Figure VII), of approximately 161. Based on this and the chemical analyses of cobalt, carbon and hydrogen, the rough formula $Co_5(OAc)_8(OH)_2$ is assigned to this compound. The formula weight is 5(160.5); the theoretical carbon and hydrogen content is 24.0% and

3.24%, respectively; which is in good aggreement with experimental results. Doremieux (14) also characterized this compound from closed vessels thermolysis of the tetrahydrate and assigned a rough formula of $Co_3(OAc)_5OH$. He also identified another new compound, obtained under these conditions, as cobalt (II) acetate dihydrate.

The formation of the third basic acetate at 280°-300°C yields a weight loss equivalent to 32.2%. However no formula can be projected because reduction to the metal and oxide formation during this transformation are deemed sufficiently great to invalidate the possible usefulness of cobalt analysis and acetic acid measurements in establishing a ratio of acetate to hydroxide. The only valid observation to be made from the work on this specie is that the source of basicity is from oxide ions rather than hydroxyl groups. This is based on the almost total lack of a O-H stretching band in its infrared spectrum. Doremieux (14) characterizes this compound and gives the rough formula $Co_3O(OAc)_4$. From physical description, temperature of formation and approximate total weight loss there is no doubt that the same specie is under consideration by both Doremieux and this work.

A general comparison between this work and that of Doremieux reveals that the dark purple specie, $Co_4(OAc)_7OH$, of this work correlates with the first plateau (Figure II) shown by Doremieux for the thermolysis in open vessels. The plateau at 34.5% weight loss with closed vessels (Fig. II), agrees with the initial compound obtained in closed vessels during this work, and is a pink compound $Co_5(OAc)_8(OH)_2$.

The final plateau (Figure II), before CoO formation, at 42.6% weight loss is in agreement with the basic acetate obtained at 290°C in this work, although the formula proposed by Doremieux can be neither proved nor disproved. However, there is agreement on the oxide rather than hydroxide anion.

The infrared spectra of these cobalt basic acetates could not be resolved to the same extent as normal metal acetates in the region of the asymmetric and symmetric stretching frequencies. Therefore, it is concluded that the broadening and possible splitting observed in this region for the compounds is due to the compounds themselves rather than the technique of the operator. There are two possible explanations for the observed splitting of asymmetric and symmetric stretching bands. The first is that these two basic acetates are not single compounds but are mixtures of two or more different compounds. The second possible explanation is that within each compound the acetate groups are in more than one structural orientation (see Figure V for acetate structures). Since the intensities of these split IR bands are practically equal and reproducable from one preparation to another, and the weight loss is reproducable over a considerable temperature range (120°-160°C), the probability for the second explanation is greater.

The magnetic susceptibility measurements indicate that the cobalt (II) is in its normal octahedral configuration with three unpaired electrons. However the orbital contribution to the magnetic moment is a little lower than expected.

IV. COBALT (II) ACETATE STRUCTURAL DETERMINATION

A. INTRODUCTION.

Cobalt (II) acetate tetrahydrate is known to have a monomeric, octahedrally coordinated structure with the unidintate acetate groups in trans positions (15). However, both nickel (II) and cobalt (II) acetates in acetic acid precipitate in a dimeric form (3,5,9), described by some as hemisolvates in which two molecules on the metal acetate combine with a molecule of solvent (3,9), while others (11) describe it as anhydrous cobalt (II) acetate. For the ternary systems (ammonium acetate, metal acetate and acetic acid) investigated by Tappmeyer and Davidson (3) and by Baird (9), it was found that the ternary compound of cobalt (II) contained two molecules of the metal acetate, and the ternary compound of nickel (II) contained four molecules of the metal acetate. The presence of two, or multiple of two, metal atoms in the salts isolated from these anhydrous acetic acid solutions indicated that possibly dimerization was involved in the formation of these compounds.

Distinct color changes have been described in the cobalt system (3,9). The anhydrous cobalt (II) acetate has a deep purple color, but the hemisolvate is light pink. The ternary compound has a characteristic maroon color. However, the purple compound previously described as anhydrous cobalt (II) acetate has been shown by Doremieux (14) and this work to be a basic acetate of cobalt. This lessens the hypothesis that color change is indicative of a considerable change in the

acetate-metal orientation.

Copper (II), chromium (II) and rhodium (II) acetates are known to have binuclear cage structures (6,7,8) in which the acetate groups act as bridges between the two metal atoms. Since dimerization was suspected in the cobalt (II) acetate isolated from acetic acid, the binuclear structure seemed to be the most logical.

Because x-ray analysis of the structure was not possible with existing equipment or time, other physical methods were investigated which, when taken collectively, should give indications as to the structure of this compound.

B. PREPARATION AND STOICHIOMETRY.

Tappmeyer and Davidson (3) described the formation of this specie as a spontaneous precipation from solutions of cobalt (II) acetate in anhydrous acetic acid. Therefore, the preparation procedure reduced to preparing as concentrated a solution as possible of the basic acetate or other cobalt acetate specie at a temperature of about 90°C and then equilibrating this solution at 100°C with a boiling water bath until the precipitation was complete (usually about 30 minutes). The solid was then filtered out and placed between porous clay plates to dry. The drying and storage was performed in a desiccator with an acetic acid atmosphere maintained over sulfuric acid by means of a beaker of glacial acetic acid. Since this specie has been characterized as a hemisolvate (3) and as anhydrous cobalt (II) acetate (11), the acetic acid atmosphere was considered critically important.

Tappmeyer and Davidson (3) in their work report that the drying and storage was done with porous plates over the mother liquor, while Liecester (11) does not comment on the handling of the compound but probably performed everything in the open laboratory. This investigator felt that the Tappmeyer and Davidson technique would not permit removal of all mechanically held acetic acid, and that working in the open laboratory could rupture any weak solvation. Therefore, maintaining acetic acid at its normal vapor pressure would assure removal of all mechanically held acetic acid and at the same time protect any weakly solvated compound which would have a lower vapor pressure than glacial acetic acid.

Analyses of the cobalt content in six seperately prepared samples of the dimer show an average cobalt precentage of 31.9% (high 32.8%, low 31.5%). Two of these samples were stored for ten days and then re-analysed for cobalt content and showed an average cobalt content of 31.6% (maximum spread between four samples was 0.7%). The theoretical content of the hemi-solvated cobalt (II) acetate is 28.5% cobalt and of the anhydrous acetate is 33.3% cobalt. There is no reason to believe that this specie is anything other than unsolvated dimeric cobalt (II) acetate, and that the crystal lattice traps up to one acetic acid molecule for every three dimeric units of cobalt acetate.

Assuming that recrystallization of the tetrahydrate from water yields a reasonably reproducible weight, several samples of the dimer were recrystallized from water and the

molecular weight was calculated. The results show an experimental molecular weight between 169 and 172. The difference between these values and the theoretical molecular weight of 177 is attributed to crystal lattice water over and above the four coordinated waters and this data is considered as supporting the unsolvated cobalt acetate specie.

C. METHODS OF ATTACK.

Magnetic moments vary characteristically with different structures and are described in the literature for tetrahydral and octahedral complexes of cobalt (II). Therefore, magnetic measurements were obtained for comparative purposes.

Johnson, Hunt and Neumann (21) found that the preparation of adducts gave valuable information. It was felt that the information obtained from adducts would tell whether additional coordination sites were available.

The positions of the infrared absorption bands of the metal acetates are well known (18,19). The exact position of these bands are dependent on such factors as the ionic character of the bonds, whether the ligands are unidentate or bidentate, and the nature of the central atom. Analysis of the position and relative intensities of the absorption bands should be a valuable aid in structure analysis.

The absorption spectra in the ultraviolet and visible region also varies characteristically for tetrahedral and octahedral complexes. However, the detailed study of the absorption spectrum of cobalt (II) acetate in acetic acid by Proll, Sutcliffe and Walkley (5) show that the spectrum of the dimer can not be measured by normal means.

Davidson and Chappel (17), as well as Tappmeyer and Davidson (3), studied freezing point determinations of solutions of nickel (II) and cobalt (II) acetates in anhydrous acetic acid. Baird (9) restudied the systems with apparent care and it was felt that further study of this was unnecessary.

The ultimate tool in structure analysis is the complete Fourier synthesis with x-ray data and subsequent Patterson or Harker projections. This is a difficult and tedious process and was not undertaken.

It was felt that proper evaluation of data obtained from the above methods would allow the investigator to draw valid conclusions concerning the structure of cobalt (II) acetate dimer isolated from acetic acid.

D. MAGNETIC SUSCEPTIBILITIES.

Since cobalt (II) complexes behave in a somewhat predictable manner with respect to magnetic properties, it was believed that magnetic moment data would allow a prediction to be made as to whether the compound is octahedral or tetrahedral.

The samples were ground as finely as possible and uniformly packed into a Gouy sample tube to a depth of 14 cm. The tube was attached to the specially adapted balance arm of the Gouy balance and positioned so that the bottom of the sample column was precisely centered between the faces of the magnet. The sample and tube were then very carefully weighed with the magnet off and then at four magnetic flux values. With the weight differences, the weight of the

TABLE V

Some Cobalt (II) & Copper (II) Magnetic Moments

Compound	Magnetic Moment* Bohr Magnetons	Magnetic Moment** Bohr Magnetons
$Co(C_2H_3O_2)_2 \cdot 4H_2O$	4.74	5.58
$Co(C_2H_3O_2)_2 \cdot 2H_2O$	4.77	------
$Co(C_2H_3O_2)_2$	------	5.12 - 5.31
$Co_2(C_2H_3O_2)_4$	4.69	------
$Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$	1.40	1.42

*This Work.
**Literature (22,23,24).

sample and known tube calibration parameters, it was possible to calculate magnetic moments by the method described in Appendix II. The magnetic moments obtained for several compounds are shown in Table V.

Cobalt (II) acetate tetrahydrate is known to be octahedrally coordinated (15), and from the magnetic data octahedral coordination is indicated for the dimeric specie, as well as the dihydrate. The critically low moments obtained for the cobalt compounds in this work are unexplainable, particularly when very good agreement with the literature was obtained for copper (II) acetate. The only remotely possible explanation would be that an undiscovered error was made in calibration of the newly constructed Gouy balance.

E. ADDUCTS.

When Johnson, Hunt and Neumann (21) prepared adducts of rhodium (II) acetate, they found that in nearly all cases two adduct molecules were coordinated onto the primary struc-

ture. In the few cases which varied, the anomalous behaviour was easily explained. Ethylenediamine, for example, is such a powerful chelating agent that the binuclear cage was disrupted.

It was believed that preparation of adducts of the cobalt (II) acetate dimer would provide useful information as to the number of coordination sites available in the structure. With this information certain structures could be eliminated as inconsistent with the data and other structures could be given added support.

Many potential ligands were attempted, both liquid and gaseous. The procedures used were as outlined by Johnson, Hunt and Neumann (21) and described in Section II, paragraph f, page 14 of this work. The summarized adduct data is shown in Table VI.

The behaviour of the ligands in forming addition compounds with the dimer were not predictable and were not always explainable. Only nitrogen coordinating ligands formed adducts.

Ammonia was the first adduct tried. At room temperature its reaction was exothermic and unpredictable. While there was a single color change initially, the weight gain showed three apparent stages at 2, 4 and 6 ligands added per dimer. The additions were not reversible on heating and those samples which showed weight gains over 2 and 4 ligands added per dimer before heating, showed slightly less than 2 and 4 ligands added after heating. The apparent stages caused the ammoniation to be performed at reduced

TABLE VI

Adducts of Cobalt (II) Acetate Dimer

Ligand	Color	# Ligands per Dimer	Reversible*
Ammonia	dark violet	1.97 - 2.58	no
	dark violet	3.60 - 5.20	no
	dark violet	5.8	no
	buff (T -18°C)	unknown**	----
Pyridine	light pink	2.40 - 3.40	no
Ethylene-diamine	light brown	3.70 - 6.30	no
Diethylamine	dark violet	1.71 - 1.85	yes
Triethylamine	no adduct	-------	----
Sec-Butylamine	dark violet	1.35 - 3.84	yes
Carbon monoxide	light blue	substitution	----
Carbon disulfide	no adduct	-------	----
Phosphine	no adduct	-------	----
Water	red	8	no
Acetone	no adduct	-------	----
Dioxane	no adduct	-------	----
Alcohol	no adduct	-------	----

*Reversible: No - Small wt. loss or decomp. @ 120°C
Yes - Original weight re-attained
**Compound unstable at room temperature, evolves NH_3

temperatures and yielded an unstable buff compound which could not be successfully identified. Further comment on this compound is made in Appendix IV.

Other amine type compounds were then tried as adducts. Ethylenediamine showed evidence indicating a complete rupture of the original structure in both liquid and gaseous

states. The apparent products were $Co(en)_2(OAc)_2$ and $Co(en)_3(OAc)_2$. Attempts at adduct formation with pyridine yielded results which can not be interpretated. Diethylamine, triethylamine and sec-butylamine (2-aminobutane) yielded no adduct in the gaseous state. When used as liquids diethylamine and sec-butylamine proved to be good solvents for the dimer. The sec-butylamine adducts, while often approaching two units per dimer, could not be stopped at this point. The extent of the addition was apparently dependent on the amount of sample which was disolved by the potential ligand. The sec-butylamine adduct was hydroscopic and had to be evaporated and stored over P_2O_5 to prevent the sample from becoming sticky. The hydroscopic characteristics of the product approaching four units per dimer were significantly greater than in the product approaching two units per dimer.

The only ligand which produced consistent results was diethylamine. This product showed only minimal tendencies to be hydroscopic and was always limited to slightly less than two units added per dimer. When the samples were covered with the liquid ligand and permitted to evaporate to dryness the end result was an approach to two diethylamine molecules added per dimer. If sufficient amounts of diethylamine were added to dissolve most of the sample, the resulting product was either light brown in color, due to probable oxidation of Co (II) to Co (III), or it was highly hydroscopic.

The hydroscopic characteristics of the amine type adducts is attributed to a rupture of the original structure but an incomplete filling of the cobalt (II) octahedral, due

to a steric inability of the bulky amines to coordinate beyond two units per cobalt diacetate. Two vacancies are therefore available to pickup water from the atmosphere.

It is noted that in some cases where adducts are formed, two unidentate ligands add. However, with most ligands the primary structure can be disrupted and further addition products result.

F. INFRARED STUDIES.

Infrared spectra were obtained with the Beckman IR5A Infrared Spectrophotometer, using Nujol and Fluorolube mulls. The use of these two mull systems proved to be highly satisfactory, since Fluorolube is transparent from 2 microns to 7.7 microns and Nujol is transparent from 7.7 microns to 16 microns except for one minor absorption band at 13.9 microns.

Resolution with the Beckman IR5A instrument was not always good. In order to obtain acceptable spectra it is necessary that the investigator take special care in preparing samples. The material to be used in the mulls must be ground to as fine a powder as possible and placed between the NaCl plates in the mull in as great a concentration as possible. The concentration of the metal acetates which yielded the best results were ones which showed 80% to 90% transmittancy in a region where the salt was approximately transparent in low concentration. Additional resolution in the area of specific bands could sometimes be obtained from more concentrated mulls by using a partial blockage of the reference beam.

TABLE VII

Cobalt (II) Acetate Asymmetric and Symmetric Modes*

Compound	This Work Asym	This Work Sym	Literature(19) Asym	Literature(19) Sym
$Co(C_2H_3O_2)_2 \cdot 4H_2O$	6.55	7.05	------	-------
$Co(C_2H_3O_2)_2 \cdot 2H_2O$	6.45	7.19	6.4**	7.2**
$Co_2(C_2H_3O_2)_4$	6.30	7.19	------	-------

*Fluorolube mull spectra in microns.
**Mallinckrodt reagent $Co(C_2H_3O_2)_2 \cdot 4H_2O$.

The infrared spectra of three cobalt (II) acetate species have been resolved: The spectrum of the tetrahydrate for comparison with the literature, and the spectra of two uncharacterized species, the dihydrated acetate (Mallinckrodt reagent) and the dimer. The asymmetric and symmetric stretching modes of the dihydrate show good agreement with the literature and indicate that Vratney and workers (19) were using dihydrate (mislabled Mallinckrodt reagent, see page 26). These values are listed in Table VII, above. No concrete deductions can be made from the observed shifting of asymmetric and symmetric stretching modes, therefore, a comparative study of the bands described as characteristic of the acetate group was undertaken.

Table VIII shows the results of this comparison for a number of metal acetates. The spectra for a number of compounds, from 5 microns to 11 microns, are shown in Appendix V. This region includes symmetric stretching, asymmetric stretching and the acetate characteristic absorption bands.

It is noted that the acetate group absorption bands

TABLE VIII

Acetate Group Infrared Absorption in Metal Acetates*

Compound	Wavelength in Microns** This Work	Literature(19)
$Ba(C_2H_3O_2)_2 \cdot H_2O$	9.54 < 9.82	9.6 < 9.8
$Cd(C_2H_3O_2)_2 \cdot 2H_2O$	9.55 < 9.85	9.6 < 9.8
$Zn(C_2H_3O_2)_2 \cdot 2H_2O$	9.45 < 9.80	9.5 < 9.8
$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	9.55 ≪ 9.70	--------
$Co(C_2H_3O_2)_2 \cdot 4H_2O$	9.48 < 9.73	--------
$Co(C_2H_3O_2)_2 \cdot 2H_2O$	9.55 ≪ 9.80	9.6 ≪ 9.8***
$Co_2(C_2H_3O_2)_4$	9.51 ≈ 9.66	--------
$Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$	9.50 ≈ 9.67	9.5 ≈ 9.7
$Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$	----------	9.5 ≈ 9.7

*Nujol mull spectra
**Relative intensity as indicated
***Mallinckrodt reagent $Co(C_2H_3O_2)_2 \cdot 4H_2O$

in the cobalt (II) acetate dimer are coincident with the wavelength of the acetate group absorption bands in copper (II) and chromium (II) acetates, two compounds with known binuclear cage structures (6,7).

G. DISCUSSION OF RESULTS.

The preparation and drying techniques used in this study were designed to determine whether or not the dimer is a hemisolvate. The results of this portion of the investigation show that only a negligible amount of solvation occures or that the crystal lattice mechanically traps small quantities of acetic acid. Since the dimer shows practically no tendency to be hydroscopic, the presence of one molecule

of acetic acid per three dimer units as shown by analysis has considerable importance. However, the major specie involved is $Co_2(OAc)_4$. This dimer specie is supported by cryoscopic studies (3,9), kinetic evidence (4) and preliminary x-ray determinations (5).

The infrared spectrum of this specie has a remarkable similiarity to the infrared spectra of the acetates known to have a binuclear cage structure, namely copper (II) and chromium (II) acetates. In addition to this, the separation of the asymmetric and symmetric stretching modes follow the predicted separation, based on Nakamoto's postulation (18) of increased separation with increased covalent bond character.

The overall indication from the adduct properties is that the dimer has two vacant coordination sites in its primary structure. However, this structure is easily ruptured by most potential ligands.

The magnetic susceptibility data indicate that the dimer specie is octahedrally coordinated. If the structure of the dimer is a binuclear cage structure, it might be expected that a suppressed magnetic moment would be observed due to metal-metal orbital overlap and partial or complete electron pairing. However, the crystal ionic radius of cobalt (II) is practically the same as that of copper (II) and the copper (II) acetate shows only a slight suppression of the magnetic moment, and still indicates one unpaired electron in spite of the proven metal-metal bond. The chromium (II) ionic radius is significantly larger than either cobalt (II) or

copper (II) and does have complete electron pairing, resulting in a diamagnetic acetate. The lack of serious suppression of the magnetic moment in the cobalt (II) acetate dimer can not be considered conclusive evidence against the binuclear cage structure.

V. CONCLUSIONS

This study varifies to some extent the thermolysis data accumulated by Doremieux (13,14). Indications for the existence of at least three basic acetates have been presented, one of which is definitely different from any characterized by Doremieux. While their exact composition could not be determined from the data of this study, parallels were shown to exist between the thermolysis of the dihydrate and tetrahydrate. These similarities might be exploited to resolve most of the intermediates formed, if TGA and DTA equipment were available.

The existence of the dihydrate came as a total and complete surprise, especially since it is mass produced by Mallinckrodt as the tetrahydrate. The only mention of the dihydrate of cobalt (II) acetate that can be found in the literature is Doremieux's (14) comment identifying it as a new compound and an initial product in the thermolysis of the tetrahydrate.

The evidence presented in this work and that presented by others (3,4,5,9) leaves no doubt in the conclusion that the specie of cobalt (II) acetate precipitated from acetic acid is a dimer. The evidence presented only in this work; magnetic moment indicating octahedral coordination, adducts showing the high probability of two vacant coordination sites, analysis yielding a formula of $Co_2(OAc)_4$ and remarkable similiarity between the infrared spectrum of this compound

and the structurally known acetates of copper (II) and chromium (II); require the conclusion that cobalt (II) acetate forms a dimer in acetic acid which has a binuclear caged structure.

Additional work should be done with the three species of cobalt acetate partially characterized in this study. Preparation procedures for the dihydrate should be solicited from Mallinckrodt, and if assistance is not recieved, laboratory work should be directed to this end. The nonhydroscopic nature of the dihydrate and the magnetic moment indicate octahedral coordination. This leads to the conclusion that there is a very high degree of probability that the dihydrate exists either as a monomer with bidentate acetates or possibly a dimer with both bidentate and bridging acetates.

Regardless of which is the true structure of the dihydrate, there now is strong evidence that cobalt (II) acetate exists in three different structural states. This will permit infrared studies which could clarify Nakamoto's (17) postulations concerning the shifting of asymmetric and symmetric stretching modes. This clarification might be accomplished by demonstrating more precisely what shifting is due to structural differences and what shifting is due to changes in the central metal atoms.

If additional acetates with binuclear cage structure are desired, I recommend that titanium (II) acetate be investigated.

This recommendation is based on a similiarity of

crystal ionic radii, Ligand-Field Stabilization Energies for octahedrally coordinated high-spin ions, and electronic structures in the divalent metals copper, cobalt, chromium and titanium. If a titanium (II) acetate dimer were found and if it were a cage structure, it would be diamagnetic. This diamagnetism is predicted because of an ionic radius slightly greater than chromium (II).

APPENDIX I

Colorimetric Analysis of Cobalt by Thiocyanate Method.

Several authors (27,28,29) describe this analytical system and outline the general procedures. Sandell (27) states the following:

> In a medium containing a sufficient concentration of ethyl alcohol or acetone, an alkali metal thiocyanate produces a blue color with cobalt, which is due to the formation of complex cobalt thiocyanates. In water solution the complex is dissociated and no color is obtained unless a very large excess of thiocyanate is present. Acetone is usually preferred to ethyl alcohol, but there is not much difference between the two solvents. According to Tomula the color intensity reached a practically constant maximum value in a medium containing 50 percent by volume of acetone (final concentration of ammonium thiocyanate 5 percent). The color intensity also depends upon the thiocyanate concentration, the increase in intensity being very rapid up to an ammonium thiocyanate concentration of 2 percent, more gradual thereafter, but still not quite constant at 10 or 12 percent (50 percent acetone solution). However, the change in intensity with thiocyanate concentration at 5 or 6 percent is so slight that one can work without difficulty at this concentration if the same amount of thiocyanate is added to unknown and standards. At 625 m , absorbance is proportional to the cobalt concentration up to at least 50 p.p.m. cobalt.

Other authors' state practically the same thing in describing the system. Dale and Banks (28) have commented on the pH range and state that it must be between 3.0 and 5.3 to obtain reproducible results. Perchloric acid and ammonium hydroxide are recommended for pH adjustment. Absorbance readings were shown to be essentially constant over a 24-hour period.

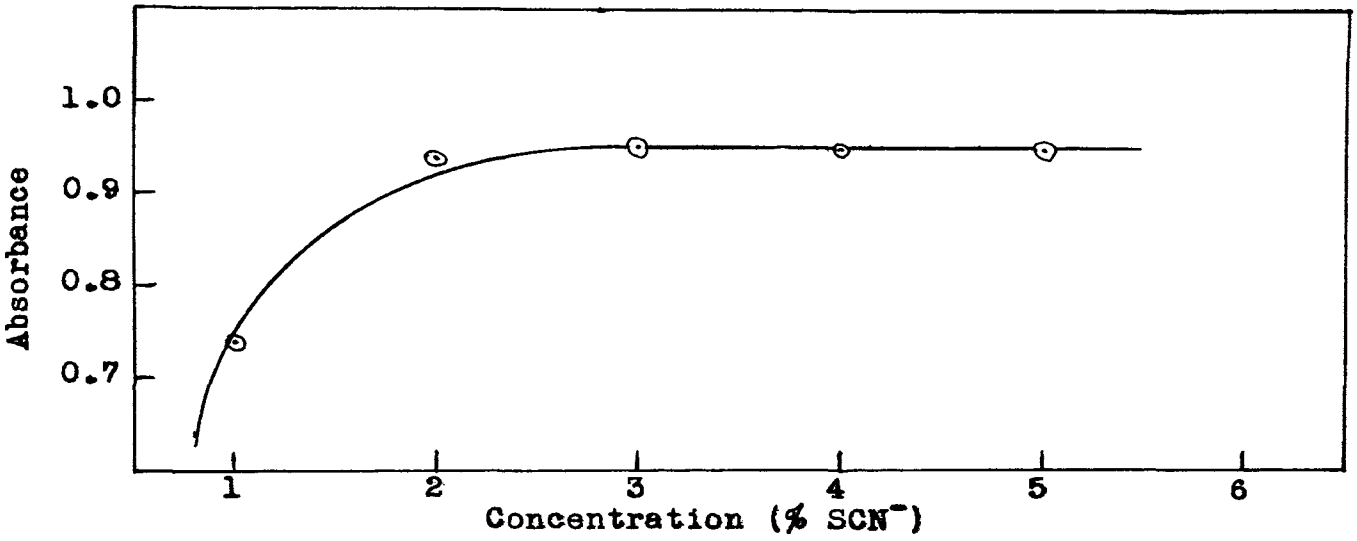

Figure VIII: Absorbance vs. Thiocyanate Concentration with 58% Acetone and 30 ppm Cobalt.

Initially this system functioned satisfactorily under the conditions of this laboratory. The reagents used were KSCN and commercial acetone instead of NH_4SCN and CP acetone recommended by Sandell. Periodically, results were obtained which were erratic and occasionally they established a trend, which appeared to be parallel to the working curve on the absorption versus parts-per-million plot.

The subsequent investigation of the analytical system showed several deviations from the literature. The thiocyanate concentration recommeded was confirmed (Figure VIII) as 5 or 6 percent NH_4SCN. This actually appears to be higher than necessary for assurance of reproducibility. Under the conditions of this laboratory 3% SCN^- (5% KSCN) final concentration was used. The critical difficulty was found to be in the volume ratio of the commercial acetone (Figure IX). The medium for measuring color intensity was therefore

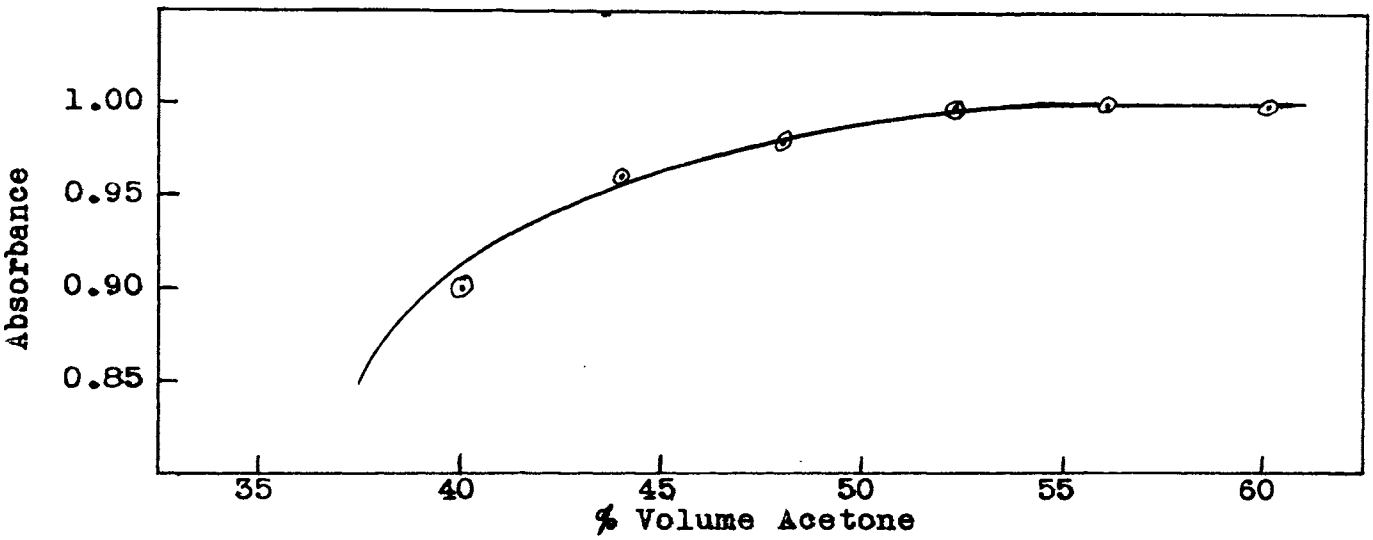

Figure IX: Absorbance vs. Acetone Concentration with 3% SCN^- and 33 ppm Cobalt.

changed to approximately 58% by volume of commercial acetone.

Small amounts of NH_4OH when added to the developed color caused significant lowering of the absorbance. While this change in absorbance may have been due to pH rather than NH_3 (NH_3 is a stronger ligand than SCN^-), it was not investigated in detail. Dilute NaOH was subsequently used to adjust pH with satisfactory results.

Final re-standardization showed deviation from Beer's law commencing at 35 p.p.m. (Figure X) while the authors' cited (27,28,29), state 50 or 60 p.p.m. are reached before deviation from Beer's law is observed. When the final cobalt concentration was less than 8 or 9 p.p.m. results also became unreliable.

The final check of the system was to investigate the color stability with time. Again, the experience in this laboratory indicated deviation from the literature, which

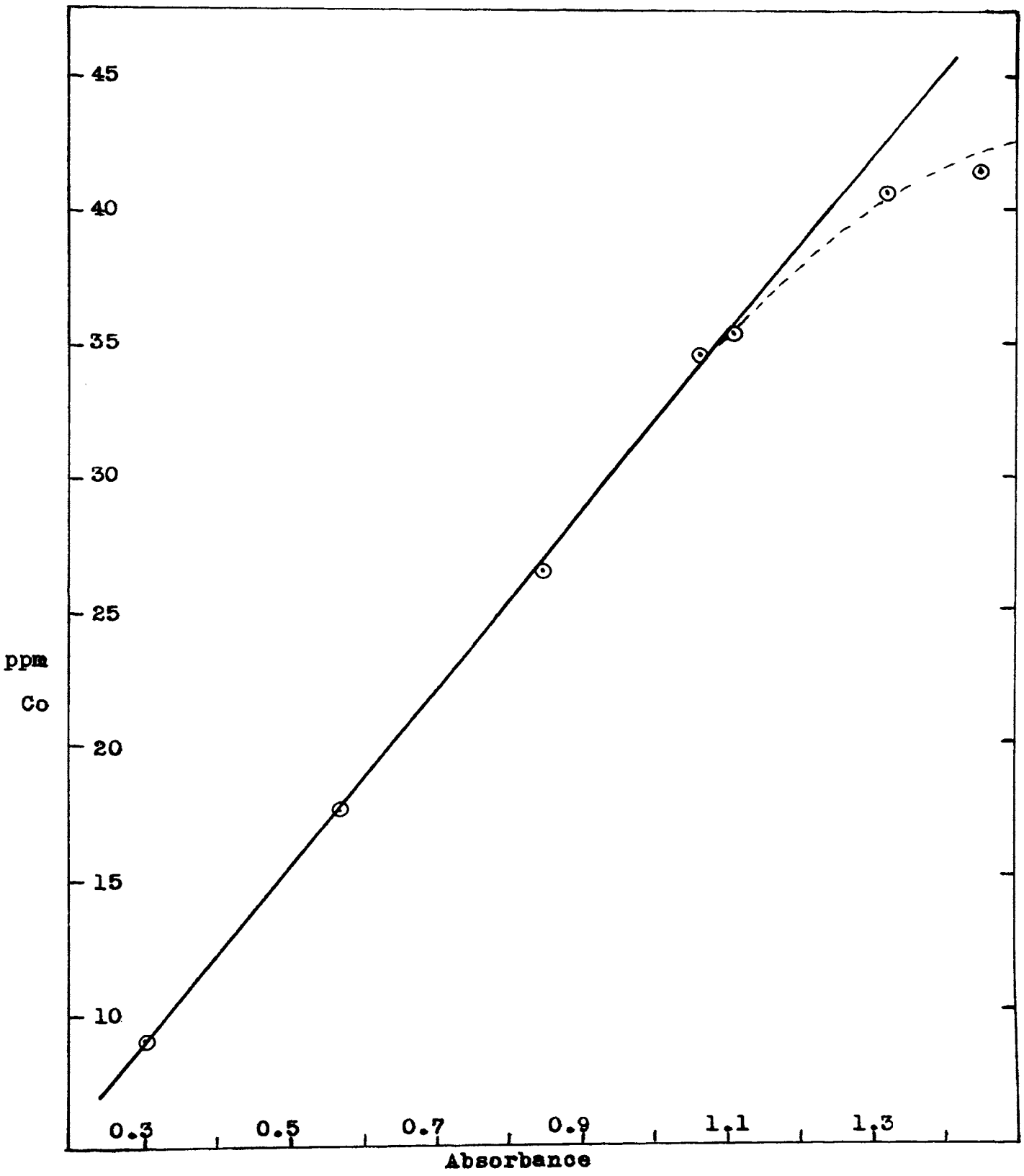

Figure X: Absorbance vs. Concentration Cobalt.

states that absorbance readings are essentially constant over a 24-hour period. It was found that after 24 hours there was a change in percent transmittance of 4 to 8% depending on cobalt concentration, and that a very small amount of light blue or colorless precipitate formed in the solutions. Another phenomenon, observed when the developed color was permitted to stand in the glassware, was retention of significant quantities of cobalt on the glass surface. No amount of washing with plain water would remove this cobalt. When fresh reagent was added to this contaminated glassware after as many as 15 water washings a color was developed showing as much as 3 to 5 p.p.m. cobalt. Periodic rinsing with nitric acid (dilute) and never permitting the cobalt thiocyanate solutions to stand in glassware any longer than necessary precludes difficulty from this effect. The interaction between cobalt thiocyanate and glass appears to be a slow reaction since the effects were not observed unless the solutions stood for 24 hours or more.

APPENDIX II

Magnetic Measurements by the Gouy Method

Particles in a magnetic field respond in two ways, by orientation to the lines of force and displacement perpendicular to the lines of force. Depending upon the response, materials are generally classified as diamagnetic, paramagnetic or ferromagnetic. In a nonhomogeneous field diamagnetic bodies displace toward decreasing field strength and paramagnetic bodies displace toward increasing field strength.

Magnetic susceptibility is a measure of this response to magnetic lines of force and is independent of field strength for diamagnetic and paramagnetic substances. Ferromagnetism can be considered, in general, a special type of paramagnetism in which susceptibility is dependent on field strength in a rather complicated way. A plot of susceptibility versus field strength for a ferromagnetic material shows an irreversible process which gives rise to a hysteresis curve.

The Gouy balance is usually used to measure diamagnetism and paramagnetism, however, with special modification it can be used to measure ferromagnetism. In the normal Gouy method a cylindrical sample of the substance of interest is suspended between the poles of a magnet so that one end of the sample is in a region of large field strength and the other end is in a region of negligible field. Data are obtained

by suspending the sample from one arm of a microbalance and measuring the apparent weight change in the sample with application of the magnetic field. The weight determinations are accomplished with the sample in a nitrogen atmosphere to eliminate the necessity to correct for the paramagnetism of oxygen in air.

Powdered samples are measured by packing them into cylindrical glass sample tubes with correction being made for the diamagnetic susceptibility of the glass. The accuracy of the measurements on powdered samples is limited by uniformity and reproducibility of packing. An accuracy of plus or minus one percent is considered very adequate.

Baird (9) describes the general calibration procedures used with this school's instrument and Selwood (30) gives a good discussion of calibration procedures, including some information on magnetic standards. These techniques will not be discussed here.

Ligand corrections, to compensate for the inherent dimagnetism of all matter, were calculated from the values given by Selwood (30) on pages 78 and 92.

In attempting to determine the magnetic susceptibility of $Co_3O(OAc)_4$, the thermolysis product formed at 290°C, a possible dependency on field strength was observed . When the change in weight with electromagnet current was plotted (Figure XI), a hysteresis type curve was observed.

Since the change in weight is a function of susceptibility and magnet current is a function of field strength, this would be expected for a weakly ferromagnetic material.

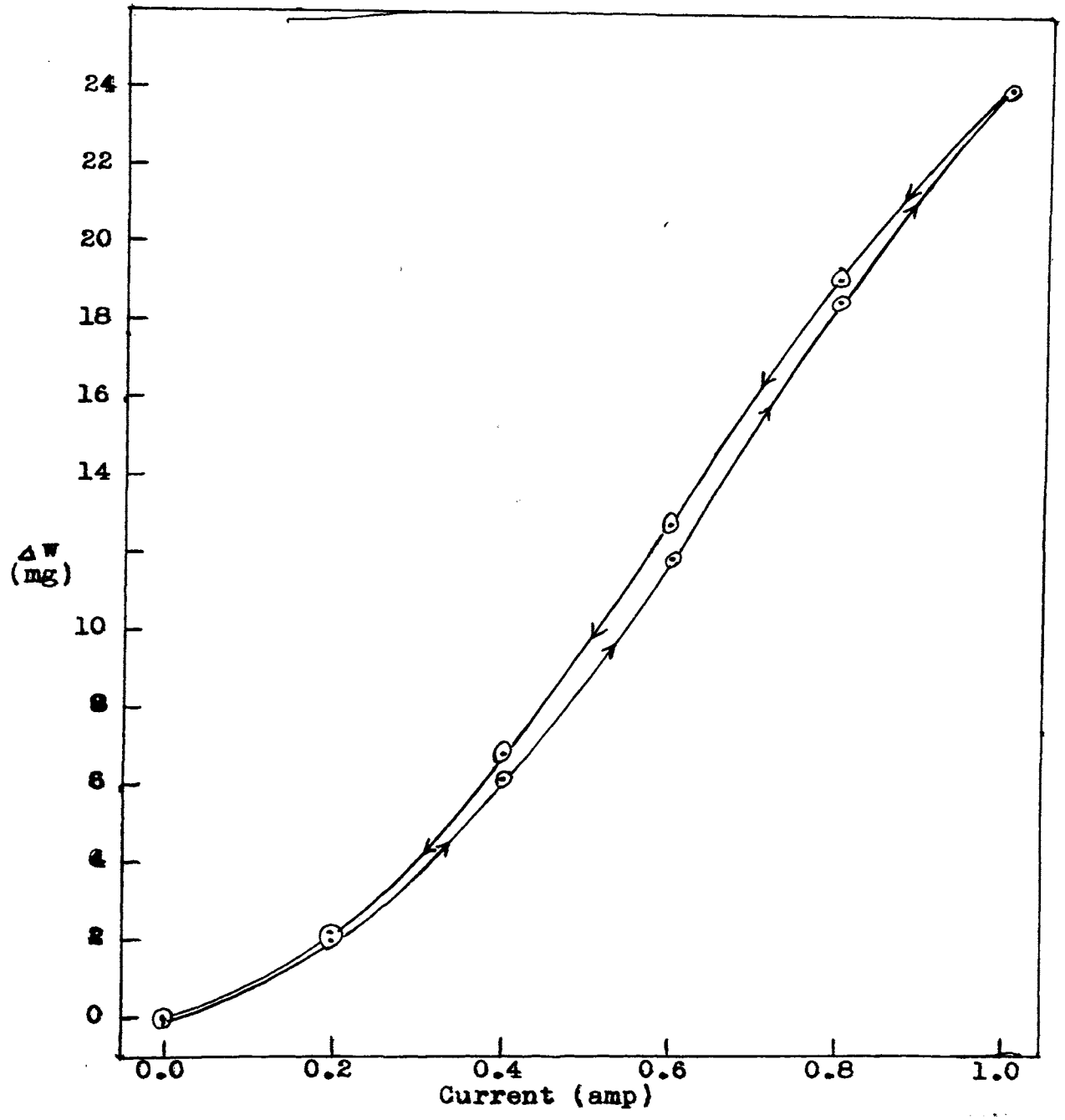

Figure XI: Change in Weight vs. Magnet Current for Thermolysis Product $Co_3O(C_2H_3O_2)_4$.

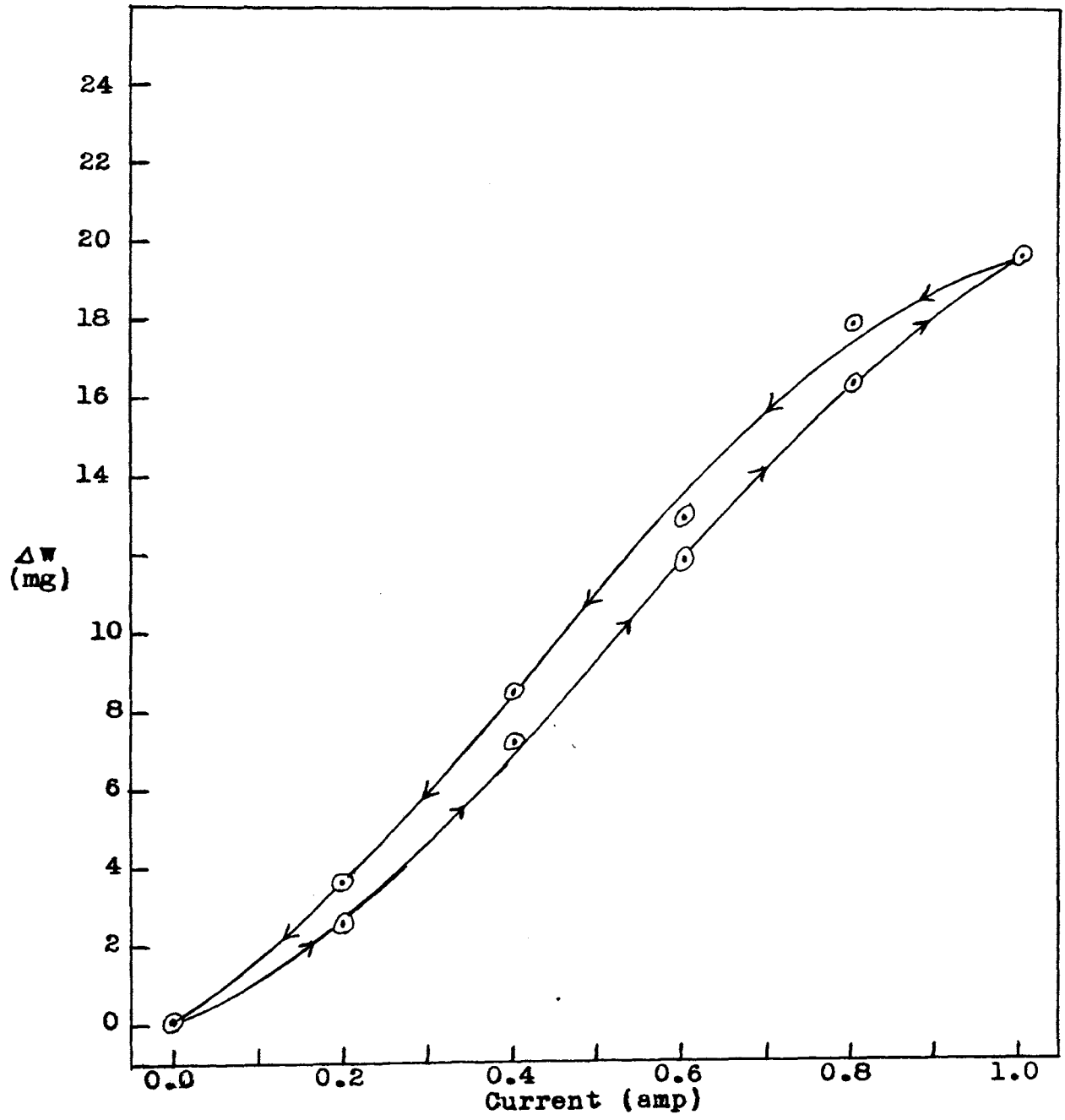

Figure XII: Change in Weight vs. Magnet Current for Fe_2O_3 in $CaCO_3$ (1/10).

To varify this, measurements were made on a known ferromagnetic material. Fe_2O_3 diluted 1 to 10 with $CaCO_3$ was used for this purpose. The results (Figure XII) confirm the ferromagnetic properties observed in the thermolysis product.

In order to determine the exact cause of this ferromagnetic behaviour additional experiments were undertaken. The expected end product of thermolysis, CoO, is paramagnetic (30), as are the hydrolysis products of thermolysis intermediates, cobalt (II) acetate and α-cobalt (II) hydroxide. Therefore, if the basic acetate is ferromagnetic the residue of hydrolysis, α-$Co(OH)_2$, will show only paramagnetic properties. If however, the residue shows ferromagnetic properties after hydrolysis is carried out under a nitrogen atmosphere to prevent any oxidation, then the cause of the observed ferromagnetism must be cobalt metal.

The results of these carefully preformed hydrolysis reactions proved the formation of some metallic cobalt during the last two stages of cobalt (II) acetate thermolysis.

APPENDIX III

Identification of Alpha-Cobalt (II) Hydroxide

The final proof of the hydroxide anion present in the proposed basic acetates of cobalt (II) is the identification of alpha-cobalt (II) hydroxide as the insoluble product of hydrolysis.

Cobalt (II) hydroxide exists in two crystalline forms (31,32). The alpha form appears as two different colors, blue and green, due to variations in particle size. The beta form is rose in color and is the stable specie. The precipation of the alpha form occures initially and after standing a period of time converts to the beta form. The conversion to the beta form is also a function of pH and if the pH is kept low the conversion of alpha to beta is almost arrested. At higher pH values the rate of conversion increases with increasing pH.

With this information concerning cobalt (II) hydroxide, the alpha form was prepared from $CoCl_2$ and NaOH for comparison with the blue material obtained from hydrolysis of thermolysis products.

After both materials had been filtered and throughly washed to remove any cobalt acetate from one and excess NaOH from the other, pH measurements of their saturated solutions were made. Both the alpha-cobalt (II) hydroxide and the unknown blue material yielded solutions with a pH of 8.1.

An infrared spectrum of the blue hydrolysis product yielded only one absorption band at 2.75 microns, corresponding to the infrared spectrum of α-$Co(OH)_2$ which was made for comparison.

Therefore, it was concluded that the blue hydrolysis product was alpha-cobalt (II) hydroxide.

The hydrolysis results and the detection of acetic acid vapors during the heating of cobalt (II) acetate require the conclusion that thermolysis products are basic acetate species of cobalt (II).

During the course of this study some additional observations of cobalt (II) hydroxide were made which had no direct bearing on the study itself and are therefore presented in this appendix.

Weiser and Milligan (32) showed evidence that conversion of the alpha hydroxide to the beta hydroxide was somewhat pH dependent, however the alpha form could only be permanently isolated by use of a stabilizer, such as mannitol. Furthermore, the solutions were never concentrated basic solutions.

In this work it was observed that when the alpha form was precipitated by using NaOH, it was difficult to obtain the alpha form free of the rose colored beta form. However, the hydrolysis of the cobalt (II) basic acetates yielded the alpha form which did not convert spontaneously to the beta form. This behaviour is anticipated from Weiser and Milligan's (32) statement that "in the presence of alkali it, α-$Co(OH)_2$, dissolves and reprecipitates in

the less soluble, stable beta mocification."

In another observation, it was seen that beta-cobalt (II) hydroxide is highly susceptible to air oxidation when not protected with nitrogen, However, the alpha-cobalt (II) hydroxide obtained from the basic acetates could stand in its mother liquor for days with no indication of air oxidation.

The possibility for an additional form of cobalt (II) hydroxide was observed in the residue of Kjeldahl analysis of NH_3 adducts. The NaOH solution used in this procedure was very concentrated (approximately a one-third volume dilution of a saturated NaOH solution) and a blue cobalt hydroxide was precipitated. This dark blue compound was remarkably stable to air oxidation and after lying on the laboratory bench for several weeks in a moist condition showed only slight signs of air oxidation.

APPENDIX IV

Products of Cobalt (II) Acetate with Ammonia and Carbon Monoxide

As already cited (Section IV, paragraph E, page 37) in this work, several unusual reactions with NH_3 and CO were observed. The purpose of this appendix is to comment on these observations which had no direct bearing on the study itself.

The attempts to form adducts with ammonia at low temperature usually resulted in the formation of a buff colored compound. This same colored compound resulted with either the dimer or dihydrate of cobalt (II) acetate. This buff colored compound appeared "dry" at the time of formation when in contact with gaseous NH_3. In addition to the color change, there was an obvious increase in volume. A reasonable estimate of the volume increase would be a product volume approximately twice that of the starting material. No weight data could be obtained due to water vapor condensation on the exterior of the reaction vessels. When this compound was permitted to warm, it would appear to melt at some temperature below room temperature but probably above 0°C and at the same time change color to a dark violet while evolving NH_3.

Limited attempts at NH_3 analyses of the buff product formed with NH_3 and cobalt (II) acetate dihydrate indicated 4.5 moles of NH_3 per mole of cobalt. The dark violet product showed about 1.13 moles of NH_3 per mole

of cobalt.

No predictions as to the nature of this compound can be made without much more extensive data.

When liquid ammonia was used, all species of cobalt (II) acetate were observed to be insoluable but they did form the buff colored compound described above. However, several other compounds were also formed and the colors of the final products at room temperature varied. The colors observed were gray, brown, light purple, dark violet and red.

Infrared spectra were obtained for only two compounds. A light purple compound was obtained from the cobalt (II) acetate dimer in liquid NH_3 and its infrared spectrum yielded seven absorption bands (3.1, 6.41, 7.17, 7.5, 9.6, 9.84 and 15 microns). This absorption spectrum indicates that the compound is definitely an acetate of cobalt with sharp asymmetric and symmetric stretching modes of the carboxyl group at 6.41 and 7.17 microns, respectively.

A light gray product was obtained with a basic acetate in liquid NH_3 and its infrared spectrum shows no evidence of being an acetate. It had four absorption bands in its spectrum at 2.8, 3.15, 6.2-6.4 (broad) and 7.1 microns.

The only conclusions drawn from these observations are that more than addition reactions occur when cobalt (II) acetate is placed in liquid NH_3 and that cobalt (II) acetate is insoluable in liquid NH_3.

When CO was attempted as a ligand, it was found that it would not add to the acetate in a normal manner. In fact

a weight loss was suffered. This addition was carried out under two sets of conditions. CO was generated by dropping formic acid onto concentrated sulfuric acid at approximately 80°C, in both sets of reactions.

Under the first set of conditions the CO was dried by a column of $CaCl_2$ and then passed over the sample in a u-tube. At room temperature no reaction appeared to occur, therefore, the temperature of the sample was raised to approximately 100°C and the reaction went to apparent completion in about six hours. The indication of reaction was a color change from red or pink to light blue, and proceded equally well with either cobalt (II) acetate dimer or dihydrate. The infrared spectrum of the product from both reactions was identical (Figure XIII), and showed that acetate was not present in the products. From this spectrum it would seem that hydroxyl and carbonyl groups are present in the products. The position of the probable carbonyl band (6.25 microns) is baffling since it does not fit any of the expected wavelengths from Cotton and Wilkinson's (33) rather complete discussion of carbonyls and their infrared absorption.

The ratio of the initial sample weight to the product weight is the same as the ratio of the starting material molecular weight to the molecular weight of a carbonyl addition and hydroxyl substituted product. This would indicate that cobalt (II) acetate dimer yielded cobalt (II) hydroxide monocarbonyl, and that cobalt (II) acetate dihydrate yielded cobalt (II) hydroxide dicarbonyl.

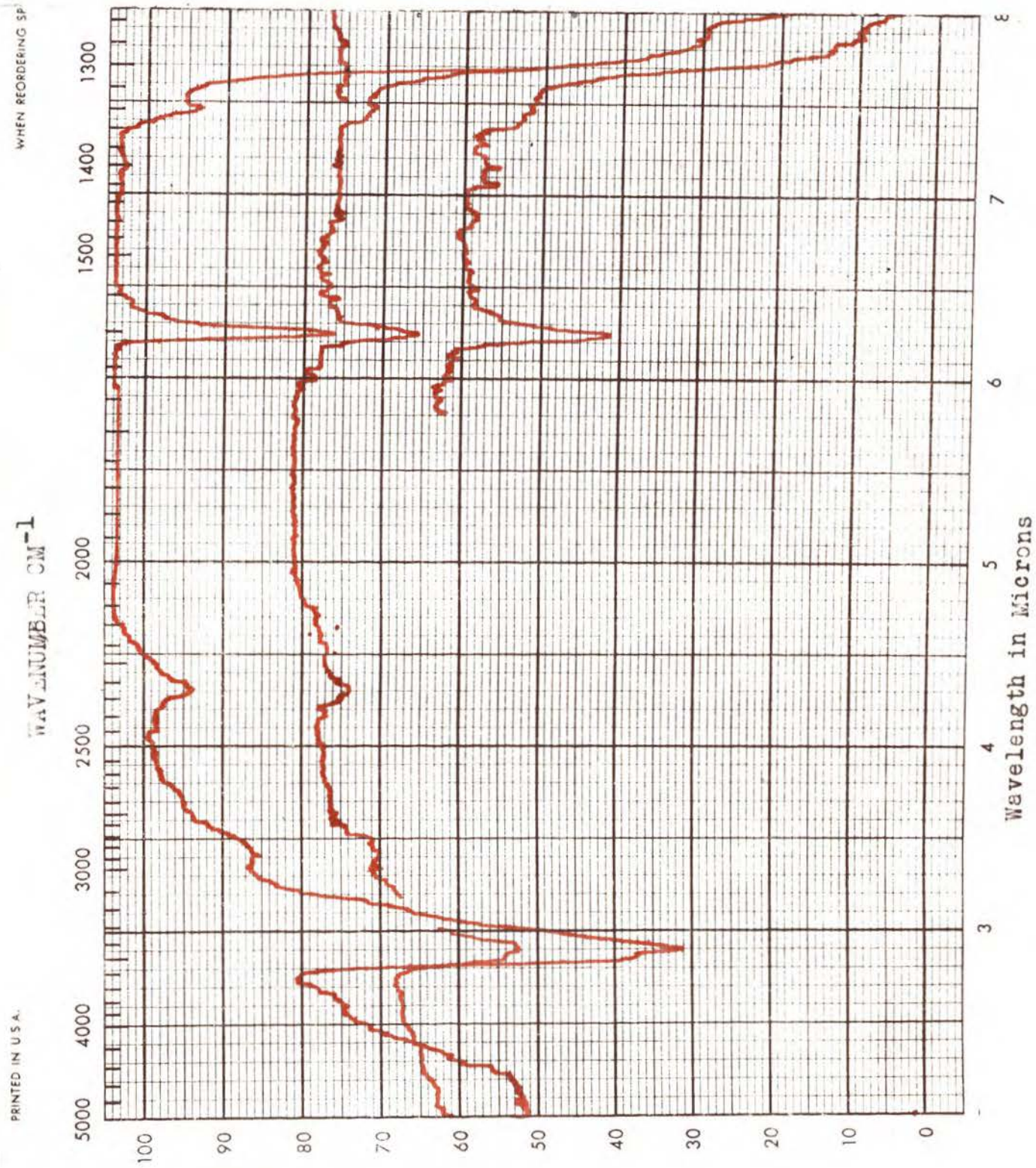

Figure XIII: Infrared Spectra of CO Adducts with Cobalt (II) Acetate.

Under the second set of conditions the CO was dried with P_2O_5 to determine if the water was coming from outside the sample. The only adduct attempted was with the dimer specie. No reaction was apparent up to a temperature of 150°C. Between 150°-200°C, some color change occurred with a small amount of light blue material appearing with a slight weight loss. However thermolysis of the acetate could be starting at this temperature and it would be safe to say that CO does not add to the dimer under any conditions.

Any conclusion from the observations of the CO reactions would be highly speculative, except to state that there appears to be a possibility that cobalt (II) hydroxide carbonyls can be formed.

APPENDIX V

Infrared Spectra

The infrared spectra of the three species of cobalt (II) acetate and of copper (II) acetate monohydrate are recorded in this appendix for reference purposes.

One observation by this worker which can not be reconciled is the apparent complicated absorption in the region of the asymmetric and symmetric stretching modes of the carboxyl group in the cobalt (II) acetates, particularly the dimer and the dihydrate (Figure XIV and XV, respectively). Cobalt (II) acetate tetrahydrate (Figure XVI) does not have the same degree of complication and Copper (II) acetate (Figure XVII) appears to be completely straight foward.

The only apparently logical explanation would be that the complication in the spectra of the dihydrate is indicative of acetate groups in two structural orientations, while the lesser degree of complication in the spectra of of the binuclear caged specie is due to small amounts of cobalt (II) acetate in other orientations. Such proposals by this author are strictly speclative, but perhaps these effects could be explained by a competent spectroscopist.

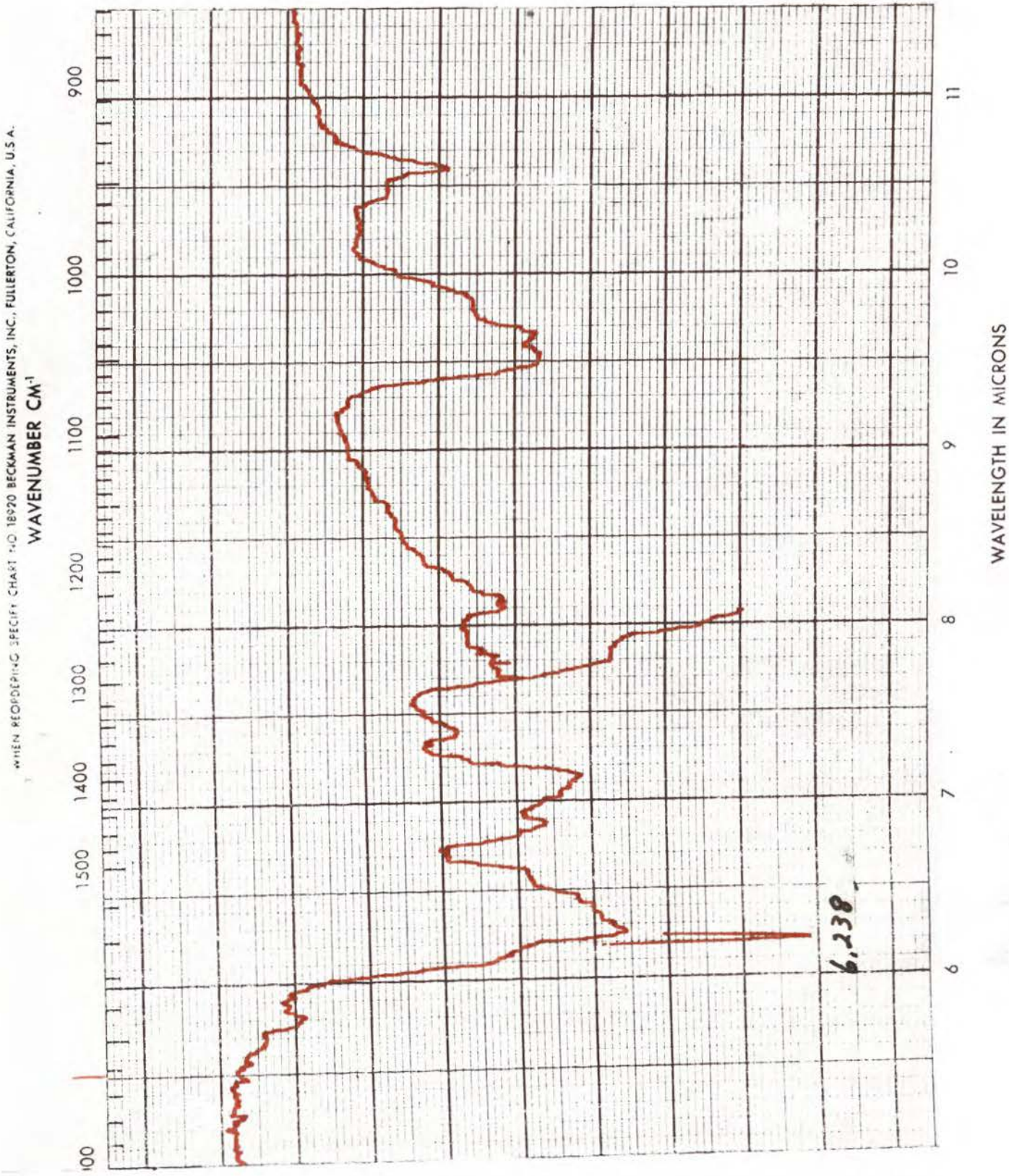

Figure XIV: Infrared Spectrum of $Co_2(C_2H_3O_2)_4$

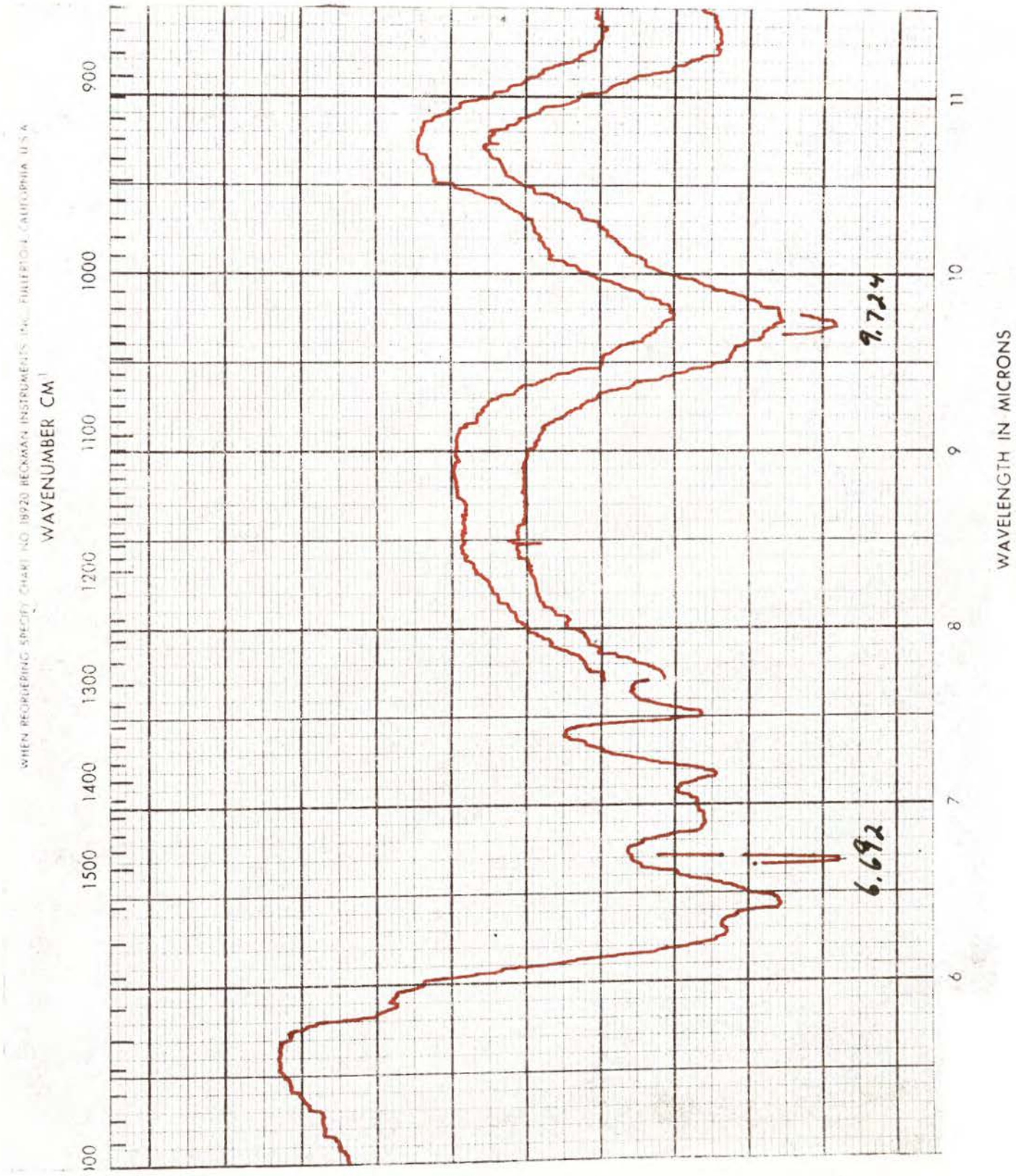

Figure XV: Infrared Spectrum of $Co(C_2H_3O_2)_2 \cdot 2H_2O$

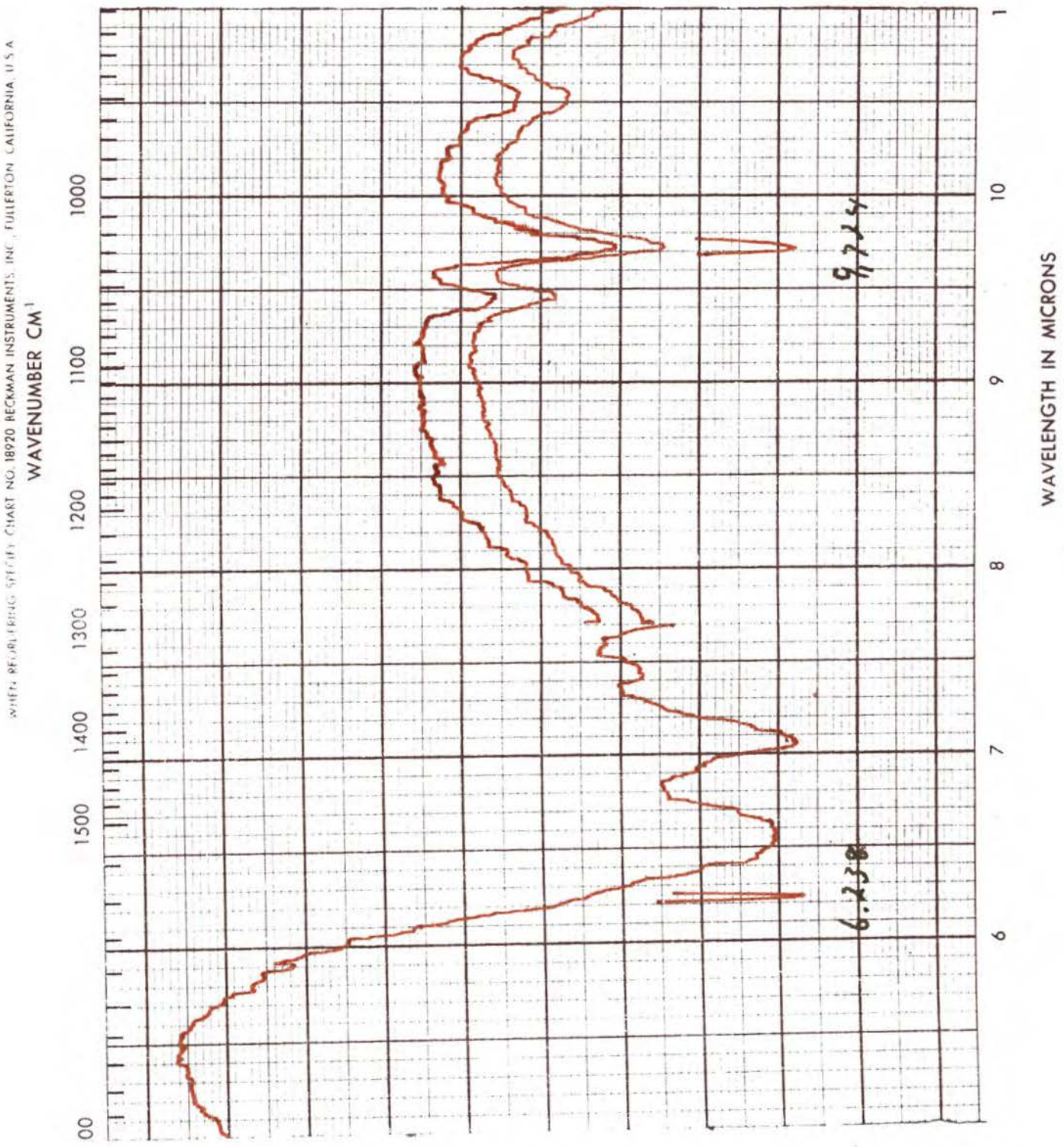

Figure XVI: Infrared Spectrum of $Co(C_2H_3O_2)_2 \cdot 4H_2O$

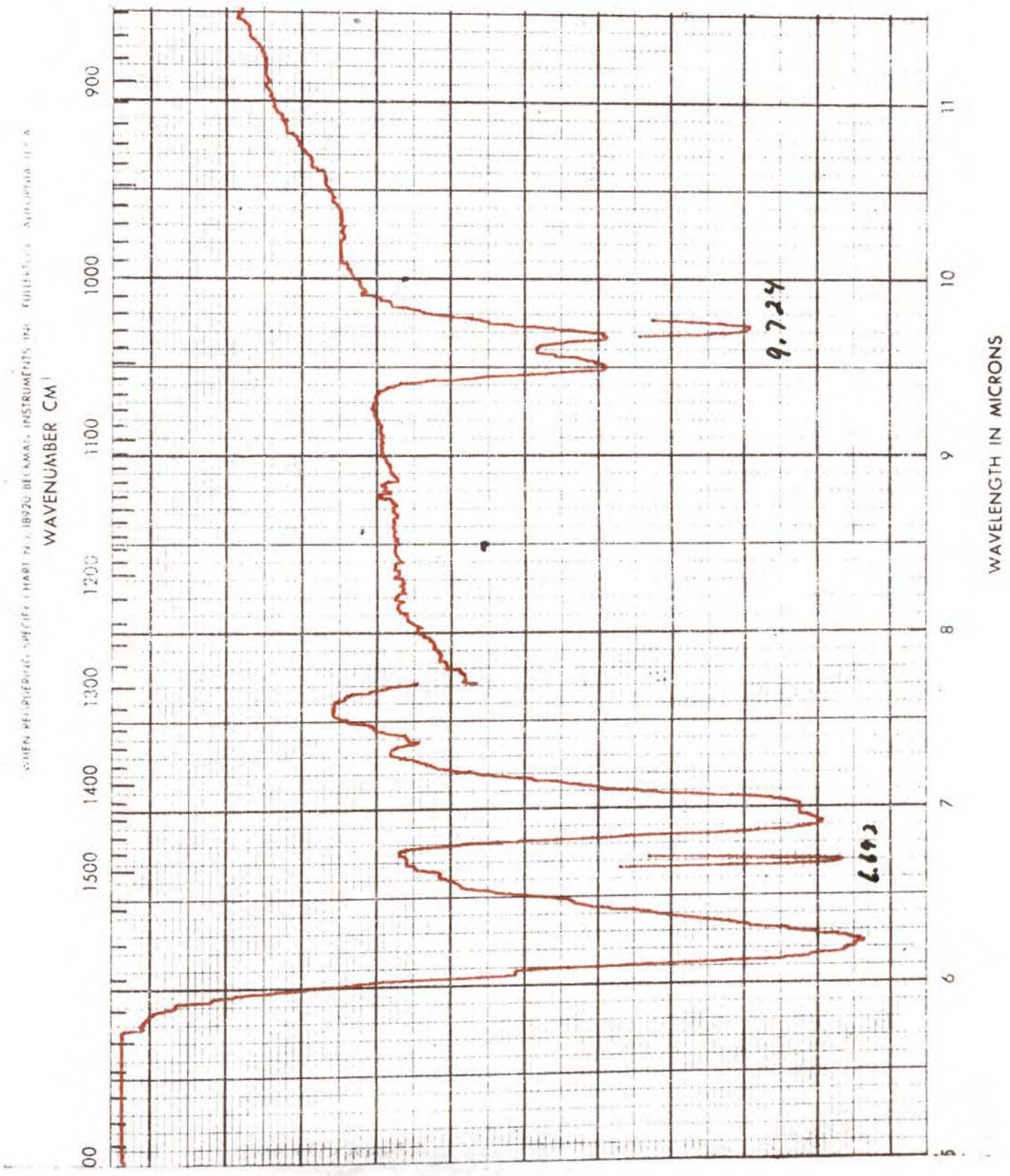

Figure XVII: Infrared Spectrum of $Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$

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VITA

Russell J. Hesch was born March 9, 1937 in Titusville, Pennsylvania, the first son of Russell and Eleanor (Southworth) Hesch.

He was graduated from Sacred Heart High School, Mount Pleasant, Michigan in 1955. He received a Bachelor of Arts degree and a Secondary Teaching Certificate from Central Michigan University in 1959.

Concurrent with the receipt of the AB degree, he was Commissioned Second Lieutenant, Regular Army and entered active service. His military assignments have included Foward Observer and Battalion Maintenance Officer with the First Howitzer Battalion, Eighth Field Artillery; Special Staff Officer, Headquarters, 25th Infantry Division; and, since September 1963 at the University of Missouri at Rolla as a graduate student in chemistry.

Captain Hesch is married to the former Catherine Ann Gross of Mount Pleasant, Michigan. The Heschs have three sons.